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Urea Manufacture

Monsanto Research Corp, Dayton, Ohio

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UREA MANUFACTURE

by

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PREFACE

The Industrial Environmental Research Laboratory (IERL) of EPA has the responsibility for insuring that pollution control technology is available for stationary sources to meet the requirements of the Clean Air Act, the Federal Water Pollution Control Act, and solid waste legislation. If control technology is unavailable, inadequate, or uneconomical, then financial support is provided for the development of the needed control techniques for industrial and extractive process industries. Approaches considered include: process modifications, feedstock modifications, add-on control devices, and complete process substitution. The scale of the control technology programs ranges from bench- to full-scale demonstration plants.

The Chemical Processes Branch of the Industrial Processes Division of IERL has the responsibility for investing tax dollars in programs to develop control technology for a large number (>500) of operations in the chemical industries. As in any technical program, the first question to answer is, "Where are the unsolved problems?" This is a determination which should not be made on superficial information; consequently, each of the industries is being evaluated in detail to determine if there is, in EPA's judgment, sufficient environmental risk associated with the process to invest in the development of control technology. This report contains the data necessary to make that decision for the air emissions from urea manufacture.

Monsanto Research Corporation has contracted with EPA to investigate the environmental impact of various industries which represent sources of pollution in accordance with EPA's responsibility as outlined above. Dr. Robert C. Binning serves as Program Manager in this overall program, entitled, "Source Assessment," which includes the investigation of sources in each of four categories: combustion, organic materials, inorganic materials, and open sources. Dr. Dale A. Denny of the Industrial Processes Division at Research Triangle Park serves as EPA Project Officer. In this study of urea manufacture, Dr. Ronald A. Venezia served as EPA Task Officer.

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ABSTRACT

This report describes a study of air emissions from the production of urea. The potential environmental effects from these emissions are evaluated.

Urea production in the United States totaled 3.45×10^6 metric tons in 1975. Major products were urea solution (38%), granulated solid material (53%), and prilled solid material (9%). Over 75% of the urea produced is consumed in fertilizers.

Both ammonia and particulates are released to the atmosphere during the manufacturing process. Major emission points are the evaporator, prilling tower, and granulator. The evaporator has the largest emission factor for ammonia, 1.73 g/kg, and the prill tower has the largest one for particulates, 3.2 g/kg.

Source severities were determined to evaluate potential environmental effects. Source severity is defined as the ratio of the average maximum ground level concentration of an emission species to the ambient air quality standard (particulates) or to a reduced threshold limit value (ammonia). Severities were between 10 and 1 for ammonia emissions from the evaporator and granulator, and between 1 and 0.1 for ammonia emissions from the prilling tower and particulate emissions from the evaporator, granulator, and prilling tower.

Emissions from the evaporator and granulator are normally controlled by scrubbers. Prill tower emissions are not controlled.

This report, submitted under Contract No. 68-02-1874 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency, covers the period from March 1976 through September 1977.

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ABBREVIATIONS AND SYMBOLS

a	--exp (B - 530/T)
AAQS	--ambient air quality standard
B	--constant in Equation 2; depending upon the nature of the surface; $0.35 \leq B \leq 0.40$
D	--distance from an emission point, m
e	--2.72
E	--emission factor, g/kg
F	--hazard factor
h	--emission height, m
m	--total number of samples
MEA	--monoethanolamine
n	--number of moles
n_i	--number of test points in the ith sample
p	--operating pressure in Equation 2, atm
p_1	--equilibrium pressure at the operating temperature in Equation 2, atm
P	--pressure of a gas, Pa
P_d	--dissociation pressure in Equation 3, mm Hg
Q	--mass emission rate, g/s
R	--gas constant, 8.3 Pa • m^3/g mole • K
s'	--surface area of ammonium carbamate deposit in Equation 2, cm^2
s_i	--standard deviation of $\bar{x}_i$ for the ith sample
s_T	--standard deviation $\bar{x}_T$
S	--source severity
t_o	--short term averaging time of 3 min
t	--long term averaging time of 1,400 min (24 hr)
T	--temperature, K
TLV	--threshold limit value
u	--average wind speed, m/s
V	--gas volume, m^3
w	--ammonium carbamate formed per hour in Equation 2, g
$\bar{x}_i$	--average of test points in the ith sample
x_i^j	--value of a point in the ith sample
$\bar{x}_T$	--average of the averages from each sample
X_1, X_2	--two general roots of the plume dispersion equation; distance from the source where $\bar{\chi}/F = 1.0$, m
χ	--ground level concentration
$\bar{\chi}_{max}$	--time-averaged maximum ground level concentration
π	--3.14

SECTION I

INTRODUCTION

Urea is produced by reacting carbon dioxide gas with liquid ammonia and dehydrating the resulting ammonium carbamate. The solution produced can then be sold directly or solidified into a prill or granule. The product is then sold in bulk or by the bag.

Urea is used mainly as a direct application fertilizer or in a mixture with other fertilizers. Urea can also substitute for natural protein in high-protein diets consumed by feedlot beef cattle and dairy cows. Urea also has industrial applications, primarily as a component in urea-formaldehyde resins. Section III of this report discusses the many manufacturing processes used to make urea solution and the various solidification processing steps, presenting operating parameters in many cases.

Section IV presents various emission parameters used to evaluate the impact of the urea industry on the environment. Emission factors for the various processing steps, as well as emission rates, average maximum ground level concentrations, and source severities for an average urea plant are given.

Section V discusses control technology currently used by and projected for the urea industry. Removal efficiencies and the potential impact of these controls on emissions are included in this section.

The last section of this report considers projected industry growth trends with special emphasis on its effect on emissions. Emerging technologies in urea production are also presented in this section.

SECTION II

SUMMARY

Total urea production in the United States during 1975 was 3.45×10^6 metric tons[a]. Major products were 1.31×10^6 metric tons of urea solutions (as 100% urea), 3.21×10^5 metric tons of prilled solid material, and 1.82×10^6 metric tons of granulated solid material. Urea was produced at 50 plant sites located in 24 states and 46 counties, parishes, or boroughs.

Urea ($CO[NH_2]_2$) is produced by the reaction of ammonia and carbon dioxide to form ammonium carbamate ($NH_2CO_2NH_4$) which is then dehydrated to form urea and water. There are over 15 production methods by which these reactions are carried out. While the basics of these processes are the same, variations occur in vessel design, operating conditions, and type and quantity of recycle of unreacted material. The aqueous solution produced by these processes contains approximately 70% urea. This solution may either be sold directly or it may be solidified.

In the solidification process, the urea solution is first concentrated by either a crystallizer or evaporator, then solidifed. If a crystallizer is used, the crystals are melted and then formed into a solid. If an evaporator is used, it produces a concentrated solution which is then solidified. In either case, solid urea is formed by prilling or granulation. Additional granular strength and packing resistance are obtained by two methods. In over 50% of the plants, formaldehyde or a phosphate-based additive is injected into the fluid material before solid formation. In the second method, the sized solid particles are coated with a clay substance. This method is used on less than 10% of all solid produced. The finished product is stored in bulk, shipped in railroad hopper cars or trucks, or bagged in 20.4-kg or 36.3-kg bags. Some urea solution may be transported to market via pipeline. Also some producers located near major waterways ship solid product by barge.

An average urea plant is located in a county with a population density of 100 persons/km^2. It has a solution capacity of 117,900 metric tons/year. The urea industry as a whole produces

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[a] 1 metric ton = 10^6 grams = 2,205 pounds; conversion factors and metric system prefixes are presented at the back of this report.

38% of its capacity as solutions, 9% as prilled solid and 53% as granulated solid. The actual operating schedule for a particular urea facility is a function of the season in its geographical region.

Emissions from urea manufacture consist of ammonia and particulates (solid urea) from the following emission points:

- Solution production
  - Bulk loading of solutions
- Solid formation
  - Evaporator
  - Prilling tower
  - Granulator
  - Bulk loading of solids

Although the prilling tower and granulator are both emission sources, they represent alternate rather than sequential process steps.

As a measure of potential environmental impact, the time-averaged maximum ground level concentration, $\bar{\chi}_{max}$, and the source severity, S, were determined for ammonia and particulate emissions from evaporation, prilling, and granulation (based on the average plant capacity, Table 1). Emissions from the bulk loading of solutions and solids are not presented in Table 1, since the source severity does not exceed 1.0 outside the average plant boundary. S for particulates is the ratio of $\bar{\chi}_{max}$ to the particulate ambient air quality standard, 260 $\mu g/m^3$. For ammonia, the air quality standard is replaced by a reduced threshold limit value, TLV®; i.e., TLV • 8/24 • 1/100.

Those persons living in the area around an average plant where the average ground level concentration ($\bar{\chi}$) of an emission species exceeds the ambient air quality standard or reduced TLV have been termed the affected population. Values for affected population also appear in Table 1.

The contribution of particulate emissions from urea plants to total national and state particulate emissions from all stationary sources was determined based on a total particulate emission factor of 0.53 g/kg from an average plant. For the urea industry the national emission burden is <0.1%. The state emission burdens for all states are <1.0%.

Existing control technology for the urea industry varies from plant to plant. In the concentration section, emissions are controlled by condensing the evaporator overheads and sewering or selling the product, or by passing the stream through a wet

TABLE 1. EMISSION PARAMETERS FROM SOLIDIFICATION PROCESSING STEPS FOR AN AVERAGE UREA PLANT[a]

Emission parameter	Evaporator	Prilling tower	Granulator
Ammonia			
Emission factor, g/kg	1.73 ± 64%	0.40 ± 84%	0.25 ± 48%
Emission rate, g/s	6.73	1.56	0.97
$\bar{\chi}_{max}$, µg/m^3	530	30.4	76.6
Source severity	8.82	0.51	1.27
Affected population, persons/km^2	245	0	22
Particulates			
Emission factor, g/kg	0.107 ± 28%	3.2 ± 17%	0.084 ± 29% to 0.20 ± 25%[b]
Emission rate, g/s	0.39	12.4	0.33 to 0.78
$\bar{\chi}_{max}$, µg/m^3	30.8	243	25.7 to 61.2
Source severity	0.12	0.94	0.099 to 0.24
Affected population, persons/km^2	0	39	0

[a]Controlled emission parameters are given for the evaporator and granulator; uncontrolled values for the prill tower, reflecting normal industry operation.

[b]Controlled emission factors for two types of scrubbers.

scrubber. In the solid formation section, control technology depends on the solid formation process used. In granulation processes, wet scrubbers are used to control emissions and recover entrained urea product. In prilling processes, ~50% of the industry uses some form of packed wet scrubber for emission control. The rest of the industry exhausts emissions to the atmosphere. Control technology to further reduce emissions has not been extensively proven. At least six companies are currently trying to develop or prove effective control technology which will reduce prill tower emissions.

Urea production is expected to increase at a rate of 4.7% to 8% per year. As a result of this growth, assuming no additional controls, emissions from the urea industry will be 32% to 59% greater in 1978 than in 1972.

SECTION III

SOURCE DESCRIPTION

A. PRODUCT DESCRIPTION

1. Physical Characteristics and Uses

Urea ($CO[NH_2]_2$) is a colorless crystal with a melting point of 132.7°C. At 20°C, it is soluble in water 1:1 and in methanol 1:6. If urea is heated above 130°C at atmospheric pressure, the principal products are biuret ($[NH_2CO]_2NH$) and ammonia. Cyanuric acid ($N_3[COH]_3$) and ammonia are the principal products above 170°C (1).

The most common end use for urea, either in liquid or solid form, is as a fertilizer. Solid urea is combined with other fertilizer materials to make multinutrient (nitrogen-phosphorus-potassium, N-P-K) mixed fertilizers. Liquid urea can be used as a direct application fertilizer or mixed with other liquid fertilizer materials. The most popular direct application fertilizer is a mixture of aqueous urea and ammonium nitrate solutions with a total nitrogen content of 32%. Other fertilizers containing urea are mixtures of various proportions of urea-ammonium nitrate-ammonia with total available nitrogen content of 32%. Other fertilizers containing urea are mixtures of various proportions of urea-ammonium nitrate-ammonia with total available nitrogen content of 37% to 49%. Other source assessment

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(1) Mavrovic, I. Urea & Urea Derivatives. In: Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Vol. 21. John Wiley & Sons, Inc., New York, New York, 1969. pp. 37-56.

documents (2-4) discuss the production of mixed fertilizers, ammonium nitrate, and ammonia.

Overall urea consumption falls into three broad categories, as shown in Table 2: fertilizers, livestock feed, and industrial feedstock (5, 6).

TABLE 2. DOMESTIC CONSUMPTION OF UREA

End use	Percent of total consumption	
	Reference 5	Reference 6
Fertilizers		
Solid	60	39.4
Liquid		38.0
Livestock feeds	25	7.7
Industrial feedstock		
Urea-formaldehyde resins	10	10.1
Melamine		
Other uses	5	4.8

Consumption statistics based on data supplied by producers to the U.S. International Trade Commission (6) differ from other reported data (5), and are based on the hypothesis that a significant portion of the urea sold as fertilizer is actually used as livestock feed. There is no way at present of verifying this supposition.

(2) Rawlings, G. D., and R. B. Reznik. Source Assessment: Fertilizer Mixing Plants. EPA-600/2-76-032c, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1976. 201 pp.

(3) Search, W. J., and R. B. Reznik. Source Assessment: Ammonium Nitrate Production. EPA-600/2-77-107i, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, September 1977. 78 pp.

(4) Rawlings, G. D., and R. B. Reznik. Source Assessment: Synthetic Ammonia Production. EPA-600/2-77-107m, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, November 1977. 82 pp.

(5) Urea. Chemical Marketing Reporter, 210(5):9, 1976.

(6) Synthetic Organic Chemicals, United States Production and Sales, 1975. USITC Publication 804, U.S. International Trade Commission, Washington, D.C., 1977. p. 195.

Urea is used in livestock feed as a substitute for natural protein in high-protein diets consumed by feedlot beef cattle and dairy cows. It is also used in urea-formaldehyde resins, and it is becoming more popular as a replacement for dicyandiamide, which was previously the primary raw material in melamine production.

2. Production

In 1975, 50 plants produced 3.45×10^6 metric tons of urea in original solution, i.e., as 100% urea (6). The average plant production rate was 69,000 metric tons/yr. No statistics are available on the exact amounts of urea produced as liquid or solid final product. It is therefore assumed that the total liquid final product is equal to that used in liquid fertilizers, 1.31×10^6 metric tons (6). Any amount of solution consumed in other applications is expected to be offset by the amounts of solid product used to make liquid fertilizers. Of the solid produced, approximately 15% (3.21×10^5 metric tons) is marketed as solid prilled product and 85% (1.82×10^6 metric tons) as solid granules (Figure 1). The derivation of this production and marketing breakdown is presented in a later section of this report.

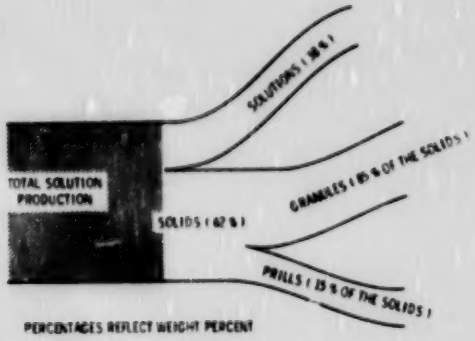

Figure 1. Physical states of urea products.

Prilled urea is of two types: standard and microprills. These differ in size, nitrogen content, level of coating, application, and end use. The prill size is governed by the spraying device used. Standard prilled urea contains 45% to 46% nitrogen. Microprills are coated, however, and their nitrogen content drops to 42% due to the extra weight added by the coating. Much of the microprill production is used in animal feed because their blending characteristics are better than those for standard prills. Standard prills and microprills are produced in the same manner. Molten urea is sprayed into a tower countercurrent to a cooling stream of air. The drops of urea solidify and form a surface crust as they fall through the air.

Granular urea is manufactured by spraying a stream of molten urea or urea solution (99.5+% urea) on a tumbling bed or falling curtain of solid urea particles. The granules are thus formed in layers. Granular urea is used mainly as a fertilizer component because of its high nitrogen content and its particle size. The rugged particles result in less degradation and dustiness during handling and transport.

3. Geographical Distribution

Table A-1 in Appendix A lists the locations (city, county, state), county population densities, and original solution capacities for the 50 plant locations responsible for 1975 production (7). Figure 2 shows the geographical distribution of these plants and indicates those facilities having more than one urea processing line. (Union Oil Company of California's plant in Kenai, Alaska, is not shown.) The plants are located in 46 counties, parishes, or boroughs in 24 states. The average county population density is 100 persons/km^2 with a range of 0.5 persons/km^2 to 696 persons/km^2.

Figure 2. Geographical distribution of urea plants.

Figure 3 illustrates the capacity distribution of the urea plants whose solution capacities are listed in Table A-1. It can be seen that 50% of the plants have a capacity at or below

(7) World Fertilizer Capacity--Urea. Tennessee Valley Authority, Muscle Shoals, Alabama, June 7, 1976. 6 pp.

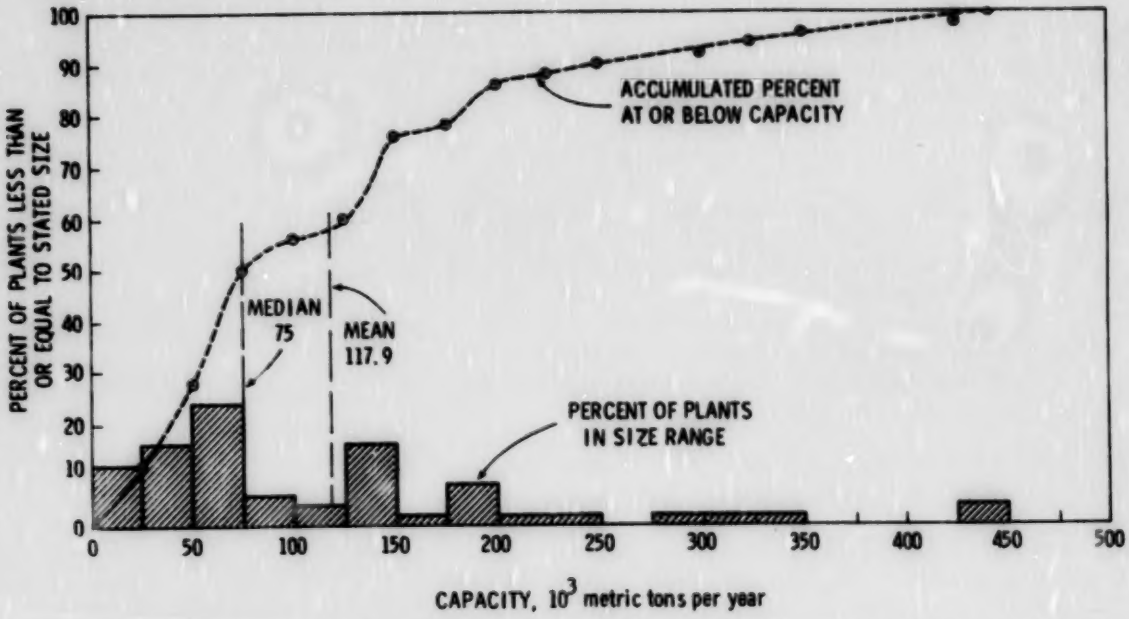
PERCENT OF PLANTS LESS THAN OR EQUAL TO STATED SIZE
ACCUMULATED PERCENT AT OR BELOW CAPACITY
MEDIAN 75
MEAN 117.9
PERCENT OF PLANTS IN SIZE RANGE
CAPACITY, 10^3 metric tons per year

Figure 3. Capacity distribution of urea plants.

75,000 metric tons/year with a statistical mean of 117,900 metric tons/year. Approximately 58% of the plants fall below the average size.

B. UREA PROCESS CHEMISTRY

Urea is produced by reacting liquid ammonia and carbon dioxide and dehydrating the resulting ammonium carbamate. A number of variables affect the degree of completion of this process.

1. Formation of Ammonium Carbamate

Anhydrous ammonia and carbon dioxide react as follows to form ammonium carbamate:

$$2NH_3 + CO_2 \rightleftarrows NH_2CO_2NH_4 \qquad (1)$$

This reaction is exothermic and spontaneous, liberating 152.1 kilojoules of heat per mole of ammonium carbamate at constant volume or 158.0 kJ/mole to 159.5 kJ/mole at constant pressure (8).

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(8) Strelzoff, S., and L. H. Cook. Nitrogen Fertilizers. In: Advances in Petroleum Chemistry and Refining - Volume 10, J. J. McKette, Jr., ed. John Wiley and Sons, Inc., New York, New York, 1976. pp. 315-406.

The rate of formation of carbamate increases approximately as the square of the pressure, all other conditions being constant. An equation to approximate this rate is given (8) by:

$$w = as'(p^2 - p_1^2) \qquad (2)$$

where[a] w = ammonium carbamate formed per hour, g
a = exp $(B - 530/T)$
s' = surface of ammonium carbamate deposit, cm^2
p = operating pressure, atm
p_1 = equilibrium pressure at the operating temperature, atm
T = operating temperature, K
B = constant, depending upon the nature of the surface $(0.35 \leq B \leq 0.40)$

The activation energy for the ammonium carbamate formation reaction is approximately 10.1 kJ/mole.

At atmospheric pressure solid ammonium carbamate will sublime at temperatures as low as 60°C, producing a mixture of ammonia and carbon dioxide. Ammonium carbamate vapor dissociation/evaporation is the reverse of Equation 1; the "vapor pressure" of ammonium carbamate is also the dissociation pressure. This dissociation pressure is reported (8) to follow the equation:

$$\log P_d = 11.1448 - 2{,}741.9/T \qquad (3)$$

where[a] P_d = dissociation pressure, mm Hg
T = temperature, °K

As a result of this high dissociation pressure, ammonium carbamate is most readily formed in the absence of water under high temperature and pressure. The importance of the elevated pressure is demonstrated by the fact that if the operating pressure is not substantially higher than the equilibrium dissociation pressure at the operating temperature, the reaction in Equation 1 will shift to the left.

2. Formation of Urea from Ammonium Carbamate

Ammonium carbamate is converted to urea and water by the following reaction with a heat input of 32.2 kJ/mole of urea:

$$NH_2CO_2NH_4 \rightleftarrows CO(NH_2)_2 + H_2O \qquad (4)$$

The water formed in the reaction limits the formation of urea solutions to a maximum of 76.93% urea by weight (8).

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[a]Units are shown as they were reported (8).

The rate of formation of the ammonium carbamate is highly dependent upon pressure. The conversion of ammonium carbamate to urea, on the other hand, is favored by high temperature. The overall yield of urea is pressure sensitive.

3. Effects of Process Variables

According to Equation 1, the molar ratio of ammonia to carbon dioxide should be 2:1. However, experiments in which two moles of ammonia and one mole of carbon dioxide were combined in an autoclave gave a urea yield of only 43.5%. Further experiments have shown that the yield can be improved by two methods: (1) raising the temperature and pressure and (2) by manipulating the molar ratio. Experiments have shown that if the excess ammonia is raised from 0% to 279%, the urea yield will increase from 43.5% to 85.2%. Raising the excess CO_2 by 300%, on the other hand, only increases the yield to 46% (8).

Excess water affects equilibrium yield (as shown in Figure 4) as well as overall functioning of the urea producing unit. It reduces the unit's productive capacity and increases the quantity of water to be evaporated, thus consuming more energy.

As a result, urea manufacturing facilities try to keep the molar ratio of water to ammonium carbamate as low as is economically and/or technically feasible. To achieve this goal at least 20 plants utilize some of the 127 kJ/mole of waste heat available from the reactions involved.

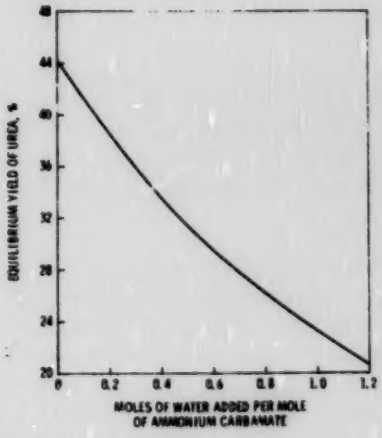

Figure 4. Effect of excess water on the yield of urea (8).

The quantity of urea which may be obtained from the overall reaction

$$2NH_3 + CO_2 \rightleftarrows CO(NH_2)_2 + H_2O \quad (5)$$

is dependent upon at least seven variables: temperature, pressure, and the concentrations of NH_3, CO_2, $CO(NH_2)_2$, H_2O, and $NH_2CO_2NH_4$ (9). When the reaction temperature, the ammonia/carbon dioxide feed mole ratio, and the water/carbon dioxide feed mole ratio are known, the equilibrium yield of urea can be calculated (8).

Urea decomposes at 60°C in an aqueous solution and the decomposition rate accelerates as temperature rises. Dry urea, on the other hand, is more stable, especially below 130°C. Decomposition products of urea include ammonia, biuret, cyanuric acid, and carbon dioxide.

Biuret is formed when solid urea is heated above 130°C at atmospheric pressure:

$$2CO(NH_2)_2 \rightarrow H_2NCONHCONH_2 + NH_3 \quad (6)$$

This reaction does not occur, however, under strong partial pressure of ammonia, such as during urea synthesis in an autoclave.

The concentration of biuret because it is phytotoxic (i.e., poisonous to plants) is kept below 0.5% in fertilizer-grade urea. Most biuret formation and decomposition occurs in the preparation of the solid urea product. The formation of biuret can be controlled, however, by holding the temperature below 130°C.

C. PROCESS DESCRIPTION

Urea is produced by the reaction of liquid ammonia and carbon dioxide gas at approximately 175°C to 200°C and 19.2 MPa to 23.2 MPa to form ammonium carbamate, which is subsequently dehydrated to form urea and water. The solution then goes to various solidification processes or is sold directly as shown in Figure 5.

This document defines urea manufacturing process as the sum of all functions which take place in the production of urea from the point where the reactants leave the feed pipe to go into a compressor or temporary holding tank until the solid and/or liquid products leave the plant. This assessment therefore includes compressors, recycle/holding tanks, reactors, condensers, absorbers, and various decomposers and strippers, where applicable, for the formation of the urea solution. In the

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(9) Frejacques, M. Les bases theoriques de la syntheses industrielle de l'uree. Chimie & Industire, 60(1):22-35, 1948.

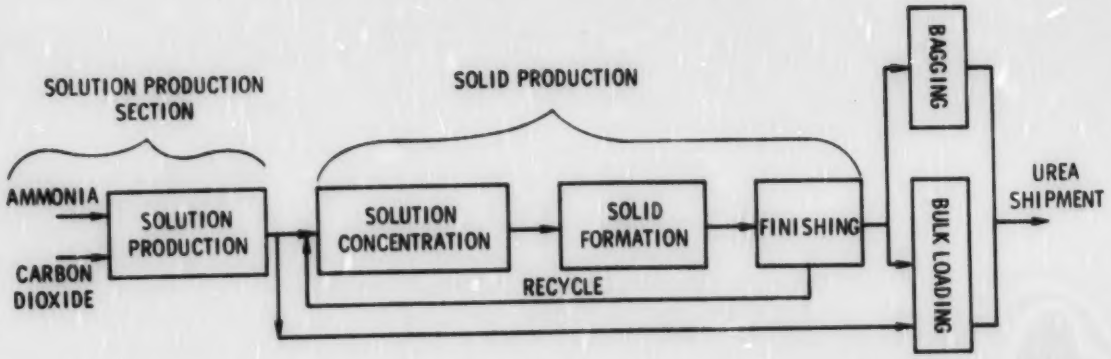


Figure 5. Block diagram of urea production process.

solid product formation process, evaporators or crystallizers and the actual particle forming apparatus (i.e., prilling tower or granulator) are included. In addition, any conveying, sizing, drying, or cooling equipment employed before the product leaves the plant is discussed.

1. Solution Production

The basic process chemistry of urea manufacturing is relatively simple. However, because operating parameters vary, particularly in the initial formation of the urea solution, numerous process designs have been utilized. Design differences occur in the separation and recycle of component streams. There are three major classes of urea processes, based on the type or quantity of recycle: once-through processes, partial recycle processes and total recycle processes.

Only a few once-through and partial recycle units have been constructed, the trend being toward total recycle systems (10). At least 75% of the urea produced today is by total recycle systems.

a. Once-Through Processes--
Figure 6 is a generalized flow diagram of a once-through urea process. While the same variables apply to once-through processes

(10) Slack, A. V. Fertilizer Developments and Trends. Noyes Development Corporation, Park Ridge, New Jersey, 1968. pp. 119-145.

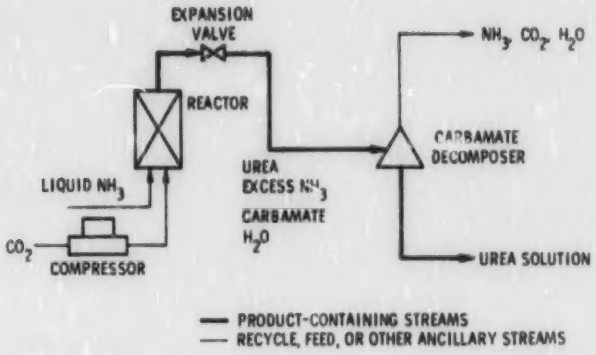


Figure 6. Once-through urea process.

as to the two recycle systems, the minor variations in actual process operation do not warrant individual discussion. Therefore a representative process description will be presented.

In once-through urea processes, ammonia and carbon dioxide are fed to the reactor and held at 175°C and 20.7 MPa for approximately 30 minutes. Approximately 40% to 45% of the carbamate will be converted to urea and water, assuming the feed streams of ammonia and carbon dioxide are in the molar ratio of 2:1 to 3:1, respectively (10).

The reactor effluent passes through an expansion valve where the pressure is reduced so that residual carbamate can be decomposed to ammonia and carbon dioxide. This process takes place in a carbamate decomposer and the resulting mixture is separated into two streams - aqueous urea and mixed gases (ammonia, carbon dioxide, and water). The aqueous urea goes for further processing or shipment. The gas stream goes directly to another fertilizer manufacturing facility as a feed stream and is therefore not considered a source of emissions.

b. Partial Recycle Process--
A refinement of the once-through process yields a partial recycle process as shown in Figure 7. This process is termed partial recycle because only excess ammonia is recovered and recycled to the reactor.

The synthesis is carried out with as much as 200% excess ammonia. This has been shown to give an equilibrium yield of urea of at least 80% (8). The reactor operating conditions are 175°C and 27.7 MPa with a residence time similar to that for the once-through process.

This process is also similar to that of the once-through process, with one additional step (Figure 7): the reactor effluent containing urea, ammonium carbamate, water, and excess ammonia

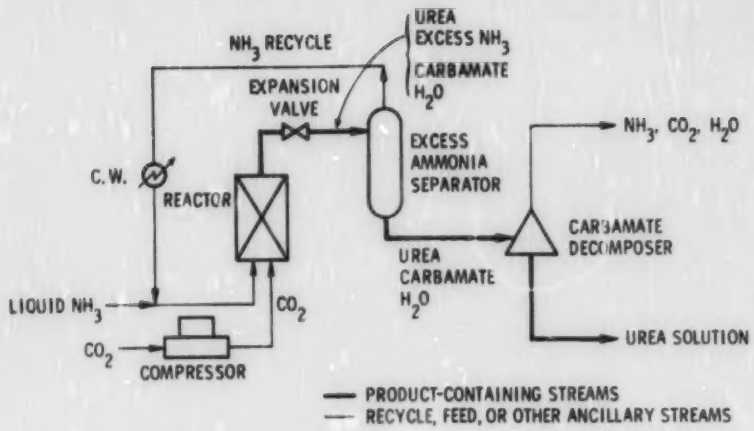


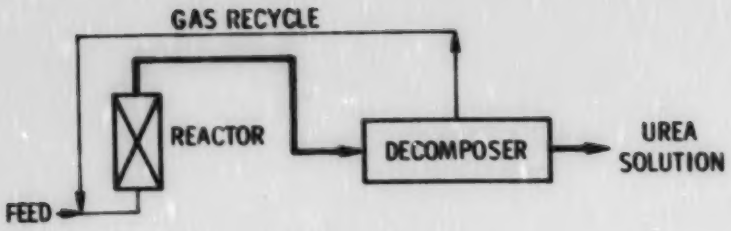
Figure 7. Partial recycle urea process.

passes through an expansion valve reducing the pressure to a few hundred kilopascals depending on the particular process design. The stream then goes to an ammonia separator where excess ammonia is removed, condensed, and recycled to the reactor. This is necessary to recover some of the cost of using excess ammonia. Also, if passed directly to the carbamate decomposer, the excess ammonia could hinder the decomposition of the carbamate.

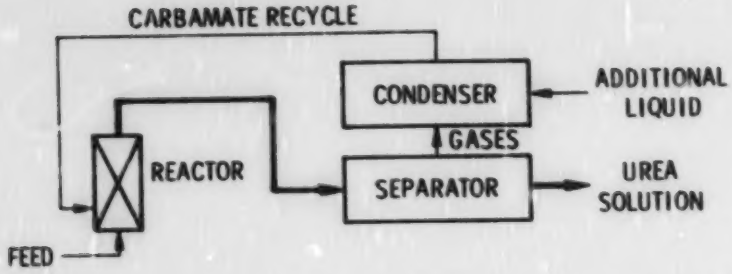
The stream containing urea, carbamate, and water goes to a carbamate decomposer which dissociates the carbamate to ammonia and carbon dioxide. The aqueous urea solution is separated and goes to further processing or shipment. The gas stream is sent to an adjunct facility as a reactant feed stream. It is not considered an emission point since no gas is emitted to the atmosphere.

c. Total Recycle Process--
The total recycle process is currently believed to incorporate the maximum operational refinements in the urea manufacturing industry and is therefore the most widely used basic process in the industry. Three variations of the total recycle process are 1) decomposed carbamate gases are separated and recycled in their pure states, 2) carbamate solution is recycled to the reactor, and 3) a combination gas/liquid recycle may occur. Incorporated in these three basic categories are at least 10 major company designs.

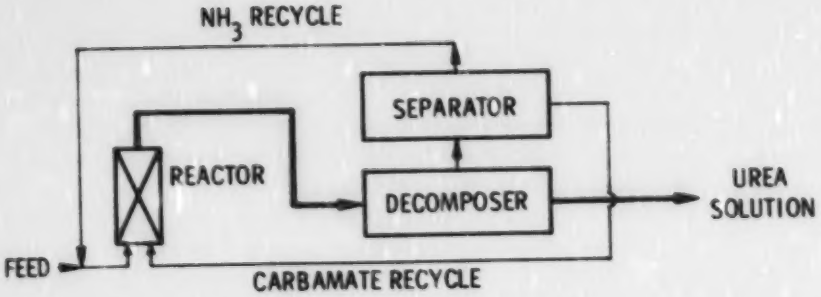
Figure 8 is an extreme simplification of the basic process differences in the three total recycle systems; gas recycle, liquid recycle, and gas/liquid recycle. These diagrams present general conceptual material flows and do not describe any particular processes.



A. Basic gas recycle process



B. Basic liquid recycle process



C. Basic gas / liquid recycle process

— PRODUCT-CONTAINING STREAMS
— RECYCLE, FEED, OR OTHER ANCILLARY STREAMS

Figure 8. Total recycle urea processes.

Figure 8a is the basic flowsheet for a gas recycle process. The material leaving the reactor is a mixture of urea, ammonium carbamate, water, and excess ammonia. This stream goes to a decomposer which separates the carbamate into ammonia and carbon dioxide. The separated gases may both be recycled, or one may be purified at the expense of the other and returned to the process. The latter resembles a partial recycle system as diagrammed in

Figure 7. In the partial recycle process, however, the excess ammonia is recovered and the ammonia or carbon dioxide in the unreacted carbamate is lost to the process. In the total recycle process, the entire quantity of ammonia is reused; i.e., excess plus decomposed carbamate ammonia. Two examples of the gas recycle process will be discussed: the CPI-Allied and Inventa processes.

Figure 8b shows the basic flowsheet for a liquid recycle process. This process is similar to the gas recycle process except that the gases are condensed with the addition of water when needed, to form a carbamate solution for recycle. Those processes whi will be discussed in this category are the Stamicarbon CO_2 Stripping, Montecatini, Pechiney, and Inventa processes.

Figure 8c gives the basic flowsheet for a gas/liquid recycle process. It is characterized by ammonia recycle with carbon dioxide being recycled in the form of carbamate. The following processes of this type will be considered: Mitsui Toatsu (Total Recycle D Improved), Stamicarbon, SNAM PROGETTI, Chemico, and Lonza-Lummus.

(1) Gas recycle processes--The CPI-Allied process, as shown in Figure 9, employs a corrosion-resistant zirconium-lined reactor which permits higher operating temperatures, i.e., from 194°C to 233°C at 30.3 MPa (11, 12). The conversion rate per pass is 80% to 85%.

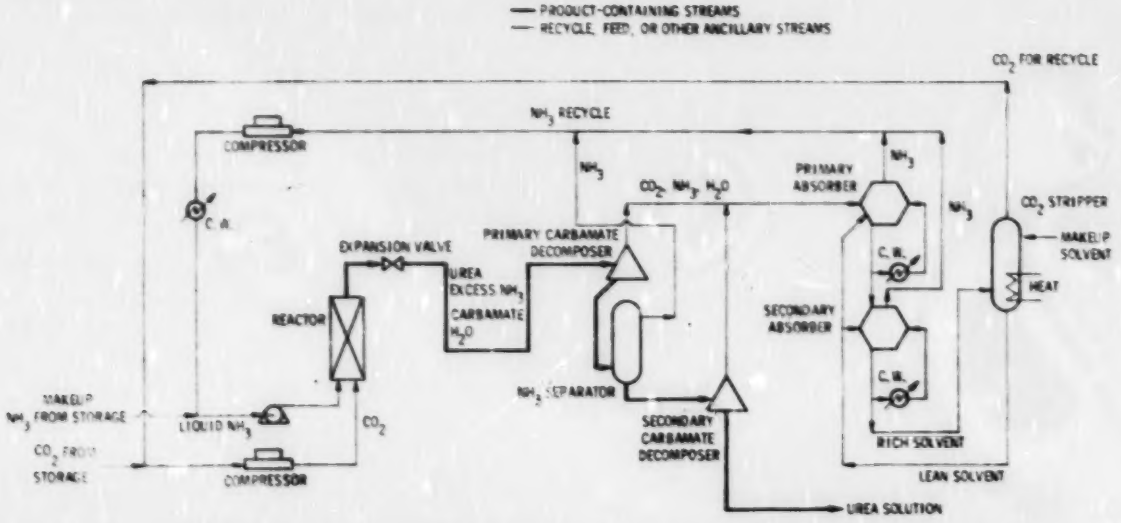


Figure 9. CPI-Allied gas recycle urea process.

(11) CPI-Allied Chemical Urea Process. Nitrogen, 47:32-33, May/June 1967.

(12) Urea Processes Today. Nitrogen, 64:17-24, March/April 1970.

This process can be used as a once-through, partial, or total recycle system. The ammonia and carbon dioxide enter the reactor in a ratio of 4:1 to 4.5:1. The excess ammonia inhibits the formation of biuret at the reactor conditions. The carbon dioxide conversion to urea is approximately 85%.

The reactor products pass through an expansion valve to a primary carbamate decomposer where 90% of the carbamate is flashed and stripped along with water vapor. The urea solution contains approximately 1.5% of the initial carbon dioxide feed. This stream is sent to an ammonia separator, where excess ammonia is stripped, and on to a secondary decomposer where any remaining carbamate dissociates at atmospheric pressure.

The overheads from both decomposers are passed through a two-unit series of absorbers where monoethanolamine (MEA) selectively absorbs carbon dioxide and water, leaving ammonia for recycle to the reactor. The carbon dioxide-rich solvent is sent to a stripper which thermally regenerates the MEA creating a rich carbon dioxide stream which is recycled to the reactor. The urea solution leaving the secondary decomposer passes through a centrifugal Min-film evaporator unit. The product contains less than 0.7% biuret and 0.20% water.

The Inventa process (see Figure 10) utilizes a reactor operating at 20.2 MPa and 180°C to 200°C (13). The molar feed ratio of ammonia to carbon dioxide is 2:1 with a maximum carbon dioxide conversion to urea of 50% (13, 14). The reactor effluent containing excess ammonia, ammonium carbamate, urea, and water passes through an expansion valve where it is lowered to 549 kPa and heated to 120°C in the carbamate decomposer (15). The ammonia and carbon dioxide go to an absorber where the ammonia is selectively absorbed and the carbon dioxide exits for recycle. The resulting ammoniacal solution of ammonium carbamate goes to a desorber to remove ammonia for recycle.

(2) Liquid recycle processes--Figure 11 is a flow diagram of the Stamicarbon CO_2 Stripping urea process. Ammonia and carbon dioxide are reacted in the molar ratio of 2.4:1 to 2.9:1 at 170°C to 190°C and 12.1 MPa to 15.1 MPa (12). The reaction product (185°C, 14.1 MPa) goes immediately to a high pressure stripper,

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(13) Cook, L. H. Urea. Chemical Engineering Progress, 50(7):327-331, 1954.

(14) Swiss Solve Urea Problems. Chemical Engineering, 59(11): 219-220, 222, 1952.

(15) Tonn, W. H., Jr. How the Competitive Urea Processes Compare Today. Chemical Engineering, 62(10):186-190, 1955.

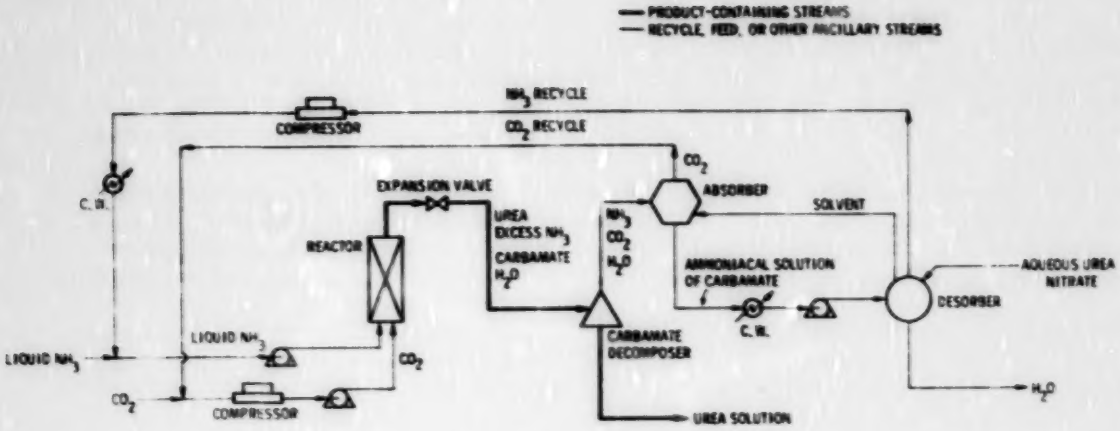

Figure 10. Inventa gas recycle urea process.

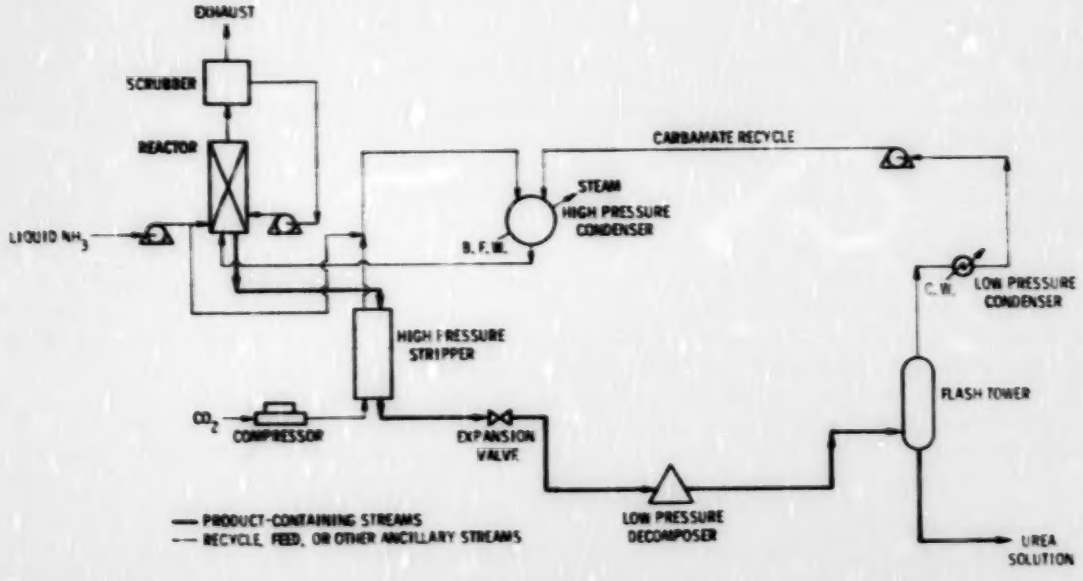

Figure 11. Stamicarbon CO_2 Stripping urea process.

operating at 14.1 MPa and 190°C (1), where the reactor stream is stripped by incoming carbon dioxide. The stream containing 15% unconverted carbamate is then let down for further decomposition in the low pressure decomposer operating at 300kPa and 120°C. The ammonia and carbon dioxide are condensed in the low pressure condenser operating at 300kPa and 60°C. The solution is pumped to the high pressure condenser where it combines with the off-gas from the high pressure stripper and a split from the ammonia feed line. The condensed stream from the high pressure condenser operating at 170°C and 14.1 MPa, goes to the reactor. An equivalent amount of 345 kPa steam is produced in the high pressure condenser and is used in other sections of the plant.

This process claims an ammonia and carbon dioxide consumption of 0.57 metric ton and 0.755 metric ton per metric ton of urea produced, respectively. Conversion efficiencies for ammonia and carbon dioxide are 65% to 85% and 70% to 85%, respectively.

Figure 12 is a flow diagram of the Montecatini process (Montedison) in which preheated liquid ammonia and carbon dioxide are compressed to 20.2 MPa and enter the reactor operating at 195°C (12, 16). The reactor mole ratio for NH_3:CO_2 is 3.5:1; for H_2O:CO_2 it is 0.6:1 (17). The effluent containing urea, excess ammonia, ammonium carbamate, and water enters a first-stage decomposer/separator operating at 8.1 MPa and 185°C. In this decomposer/separator most of the ammonia is driven off along with the carbamate decomposition products. This stream, along with 20% to 30% of the carbon dioxide feed stream, is fed to the first-stage carbamate condenser which operates at 8.1 MPa and 145°C.

The effluent from the first-stage condenser passes to an auxiliary condenser operating at the same pressure but at 115°C so that condensation is completed. The gas leaving this condenser is washed to remove ammonia. The liquid stream is recycled to the reactor.

The liquid stream leaving the first-stage decomposer/separator proceeds to a second-stage unit operating at the same temperature as stage one and 1.2 MPa, and finally to a third stage operating at 202 kPa to 303 kPa before leaving the facilities. The gaseous effluents from the stage two and three decomposer/separators are condensed in carbamate condensers three and four, respectively. In condenser three the gas stream is mixed with

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(16) Borelli, T., and G. Nardin. Procede Montecatini Edison pour la production d'uree de gros tonnage. Chimie et Industrie - Genie Chimique, 104(16):2017-2022, 1971

(17) Montecatini Edison's New Total Recycle Urea Process. Hydrocarbon Processing, 49(8):111-112, 1970.

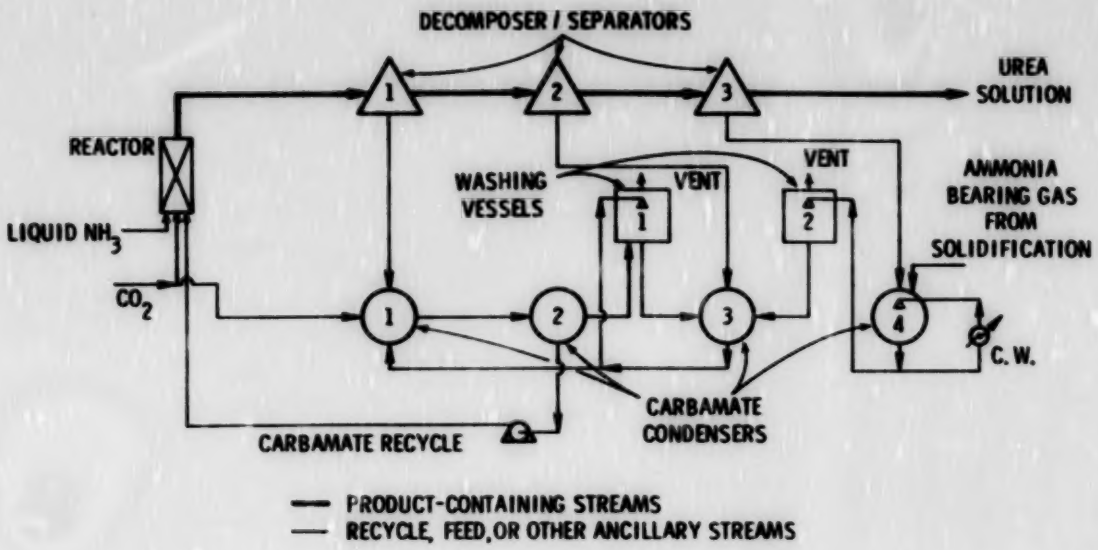

Figure 12. Montecatini complete recycle urea process.

liquid effluent from both wash vessels and the liquid carbamate is sent to the first-stage condenser. In condenser four an ammonia-bearing gas stream from the solidification section is washed with cold ammonium carbamate, and the resulting effluent is cycled through a wash vessel before going to condenser three.

In the Pechiney total recycle process (Figure 13), a neutral mineral is incorporated to act as a "heat sponge," as a medium for recycling unreacted ammonia and carbon dioxide, and as a corrosion inhibiter. Ammonia and carbon dioxide are fed to the reactor operating at 20.2 MPa to 20.6 Mpa and 177°C to 183°C (13, 15, 18). In the carbamate stripper and decomposer, 40% to 50% conversion of carbamate to urea is achieved; the remaining carbamate is decomposed to ammonia and carbon dioxide which go to an agitated slurry vessel where they recombine to form ammonium carbamate in an oil slurry. This slurry is then recycled to the reactor. The urea-oil mixture leaving the carbamate stripper and decomposer goes to an oil decanter which separates the oil from the mixture to supply the slurry vessel. The urea goes for further processing.

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(18) Urea Via the Pechiney Process. Chemical Engineering, 62(4):320-323, 1955.

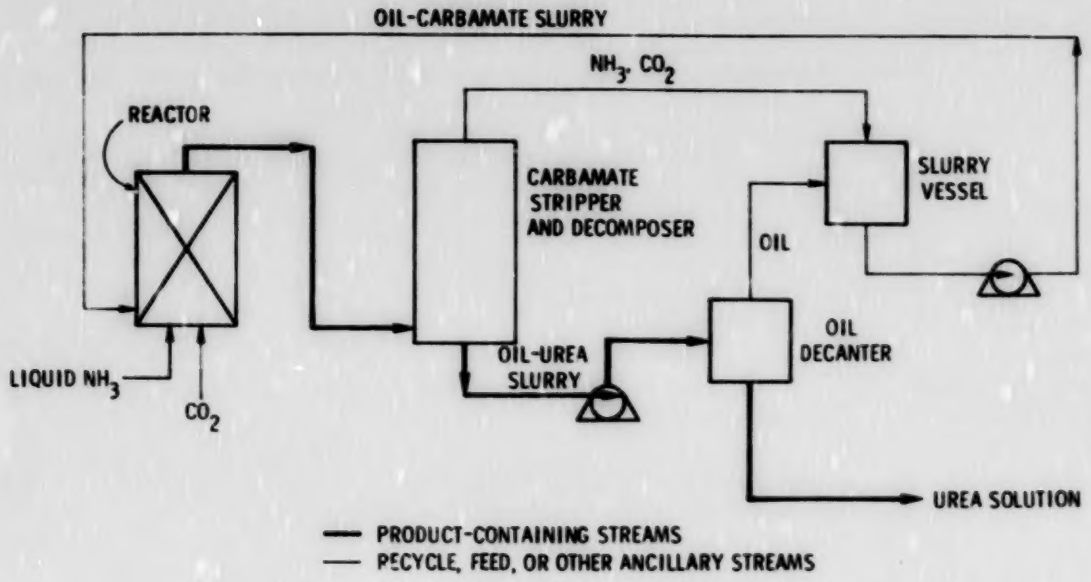

Figure 13. Pechiney total recycle urea process (oil slurry).

In addition to the gas recycle process previously described, Inventa also has a liquid recycle process, as shown in Figure 14. In this process, the reactor operates at 185°C and 23 MPa with a molar ratio of NH_3/CO_2 = 3.5 to 4.0/1 and a conversion of 62% to 65% (1). The reactor effluent is expanded to 505 kPa and heated to 120°C, after which the liberated ammonia and carbon dioxide are fed to a primary absorber (at the same pressure but at 50°C) where an aqueous ammoniacal carbamate solution is formed. This solution goes through a heat exchanger to remove the heat of reaction before being sent to the desorber operating at 140°C to 150°C and 5.05 MPa where the carbamate is once again decomposed to remove some of the water before recycling to the reactor. The absorber gaseous effluent is passed to the secondary absorber operating at 5.05 MPa and 90°C where it is condensed to the carbamate solution and sent to the reactor. Water resulting from the operation may either be used elsewhere in the plant or sewered, depending on the particular installation.

(3) Gas/liquid recycle processes--The Mitsui Toatsu urea process is actually several processes in one: 1) once-through process with a carbon dioxide conversion of 82% and ammonia conversion of 34%, 2) an ammonia partial recycle (56% conversion of NH_3) or 3) a partial recycle with 80% carbon dioxide conversion and 70%

ammonia conversion. There are also two total recycle processes and an integrated process where the ammonia synthesis loop and the urea facilities are tied together for heat economy (19).

Shown in Figure 15 is the Mitsui Toatsu Total Recycle D Improved urea process. Another total recycle process, labeled "C," does not incorporate the medium pressure decomposer and absorber but

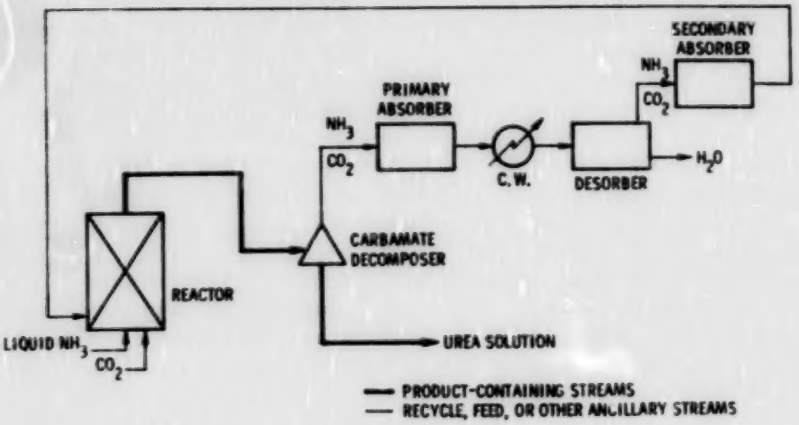

Figure 14. Inventa liquid recycle urea process.

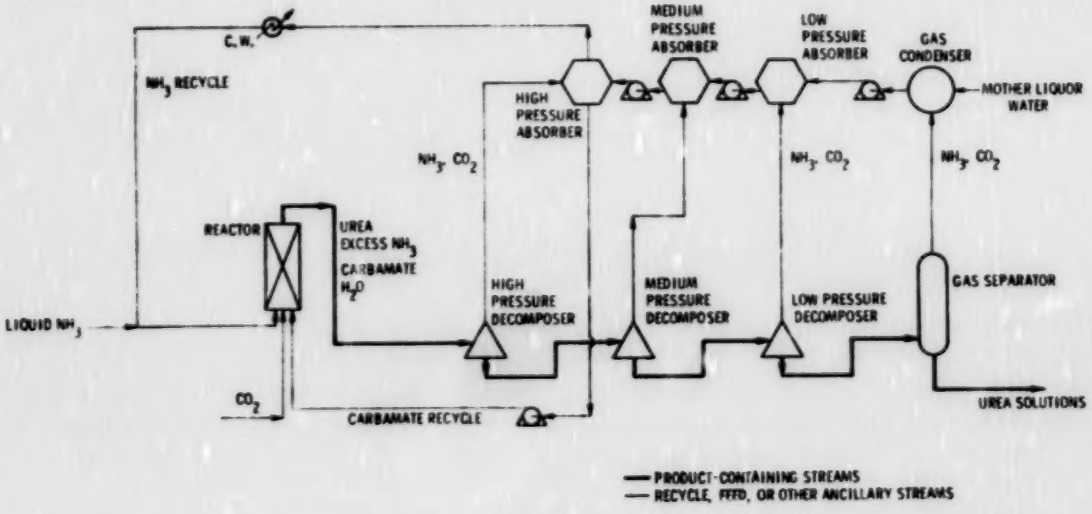

Figure 15. Mitsui Toatsu total recycle D improved urea process (Toyo Koatsu).

(19) Urea (Mitsui Toatsu Process) - The M. W. Kellog Co. Hydrocarbon Processing, 50(11):215, 1971.

is otherwise the same (20). In the process shown, the reactor is fed with a molar ratio of ammonia to carbon dioxide of 4.3:1 and operated at 190°C and 24 MPa. Approximately 67% conversion to urea is obtained (1).

The reactor effluent goes to the high pressure decomposer, operating at 150°C and 1.8 MPa then to the medium and low pressure units operating at 410 kPa and 130°C, and 101 kPa and 120°C, respectively (20). The gaseous effluents from these decomposers go to their respective absorbers where the ammonia and carbon dioxide contact with the condensate from the previous stage resulting in a lower water content in the carbamate recycle. In the high pressure absorber, excess ammonia is stripped for recycle, and the condensed carbamate is recycled to the reactor.

The Stamicarbon total recycle process is shown in Figure 16 (20). The reaction takes place at 20.2 MPa and 170°C to 190°C. The reactor effluent is lowered to approximately 505 kPa before going to the preseparator. The liquid stream from the preseparator passes through two additional separation steps before finally leaving the process. The various ammonia and carbon dioxide streams are condensed, and the carbamate formed is recycled to the reactor. A wet scrubber is used on the gas stream to recover ammonia for recycle.

The SNAM PROGETTI urea process, as shown in Figure 17, is similar to the Stamicarbon CO_2 stripping process, but the stripping is done by ammonia rather than carbon dioxide. SNAM PROGETTI also has a process which can be integrated with ammonia synthesis (21). The process, as shown, can operate at two different reactor pressures, 13 MPa to 16 MPa or 20.2 MPa to 25 MPa (1, 12, 22). The normal operating temperature in the reactor is 180°C to 190°C. The normal molar feed ratio of ammonia to carbon dioxide is 3.3 to 3.5:1 (23, 24). The feed is obtained from carbamate

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(20) Yoshimura, S. Optimize New Urea Process. Hydrocarbon Processing, 49(6):111-115, 1970.

(21) Pagani, G., and U. Zardi. Integrate for Lowest Urea Cost. Hydrocarbon Processing, 5(11):125-129, 1972.

(22) Pagani, G., and U. Zardi. SNAM PROGRETTI Stripping Technique: One Basic Principle for Two Methods of Producing Urea. Presented at the 74th National Meeting of the American Institute of Chemical Engineers, New Orleans, Louisiana, February 1973. 16 pp.

(23) Zardi, U., and F. Ortu. Recycle Carbamate Via Ejector. Hydrocarbon Processing, 49(4):115-116, 1970.

(24) Urea - SNAM PROGRETTI. Hydrocarbon Processing, 54(11)210, 1975.

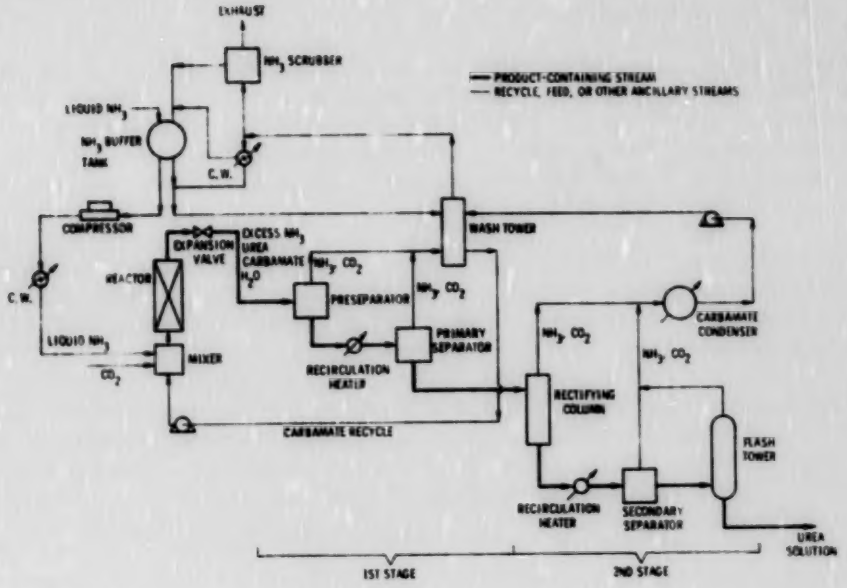

Figure 16. Stamicarbon total recycle urea process.

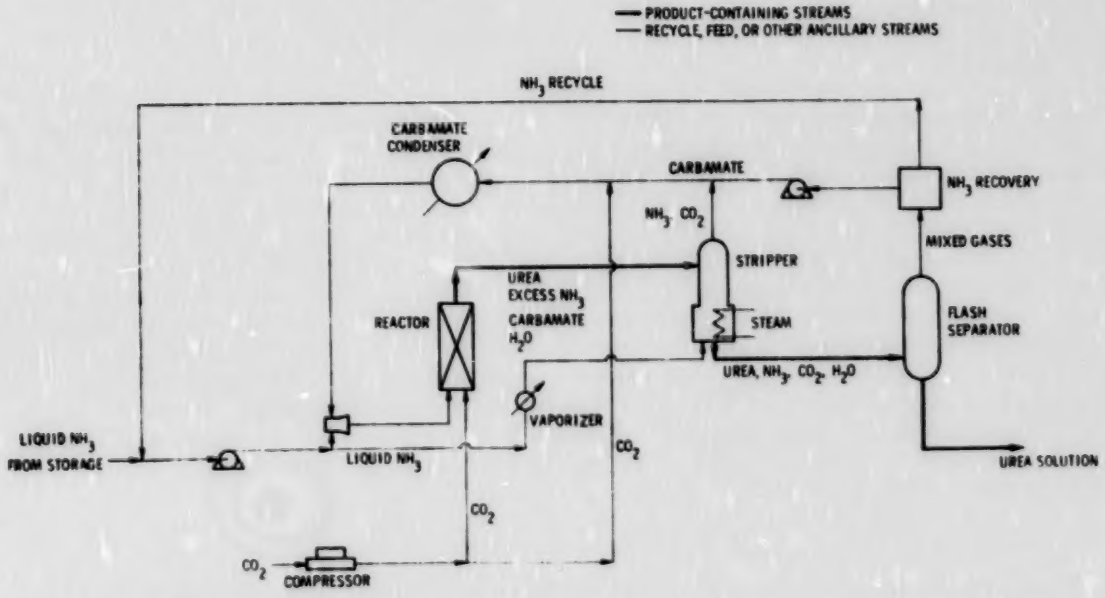

Figure 17. SNAM PROGETTI Ammonia Stripping urea process.

recycle by using an ammonia-driven ejector and straight carbon dioxide. Under these conditions a 60% carbon dioxide conversion per pass can be obtained.

The effluent leaving the reactor is passed to a stripper operating at 10 MPa to 15 MPa and 160°C to 200°C (24). Most (>90%) of the ammonia and carbon dioxide are removed in the stripper with the remainder being removed in the flash separator. These overheads are collected and the carbamate is recycled; excess ammonia is also recycled to storage.

The unique feature in the SNAM PROGETTI process is the carbamate ejector which introduces carbamate and ammonia to the reactor (21). The ammonia pressure drop through the ejector of 41 MPa supplies the necessary driving force.

The Chemical Construction Corporation - U.S.A. (Chemico) has developed the Chemico total recycle urea process shown in Figure 18. Chemico is also the United States licensed contractor for the SNAM PROGETTI (25). In the process shown in Figure 18, ammonia and carbon dioxide are fed in a molar ratio of 4:1 to the reactor operating at 19 MPa to 23 MPa and 175°C to 200°C (1, 12). Under these conditions a carbon dioxide conversion of 64% to 70% per pass can be achieved. The reactor effluent goes through two stages of purification and recovery of ammonia and carbon dioxide. The first stage operates at 2.0 MPa to 2.5 MPa and 155°C. The overheads from this stage go to the secondary absorber and the liquid effluent goes to the second stage for further purification. The second stage operates at 202 kPa and 120°C. The process stream leaving the process contains 74% to 75% urea and 25% to 26% water.

The Lonza-Lummus urea process shown in Figure 19 employs a molar feed ratio of ammonia to carbon dioxide of 4.5:1 (1). The reactor is operated at 30 MPa and 200°C. At these conditions, a carbamate conversion of 70% can be achieved. The reactor effluent is pumped to the first-stage decomposer which operates at 1.5 MPa and 150°C (1, 26). The liquid effluent continues through two additional purification stages. The gaseous effluents from the first-stage decomposer go to the first-stage absorber where the excess ammonia is separated and the carbamate is recycled. The gaseous effluents from the third decomposer go through the corresponding absorber, and the effluent from this absorber goes to the second-stage absorber. The liquid effluent from the second-stage absorber is recycled to the first-stage decomposer for repurification.

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(25) Urea Production. Nitrogen, 91:44, September/October 1974.

(26) The Lonza-Lummus Urea Process. Nitrogen, 33:31-32, January 1965.

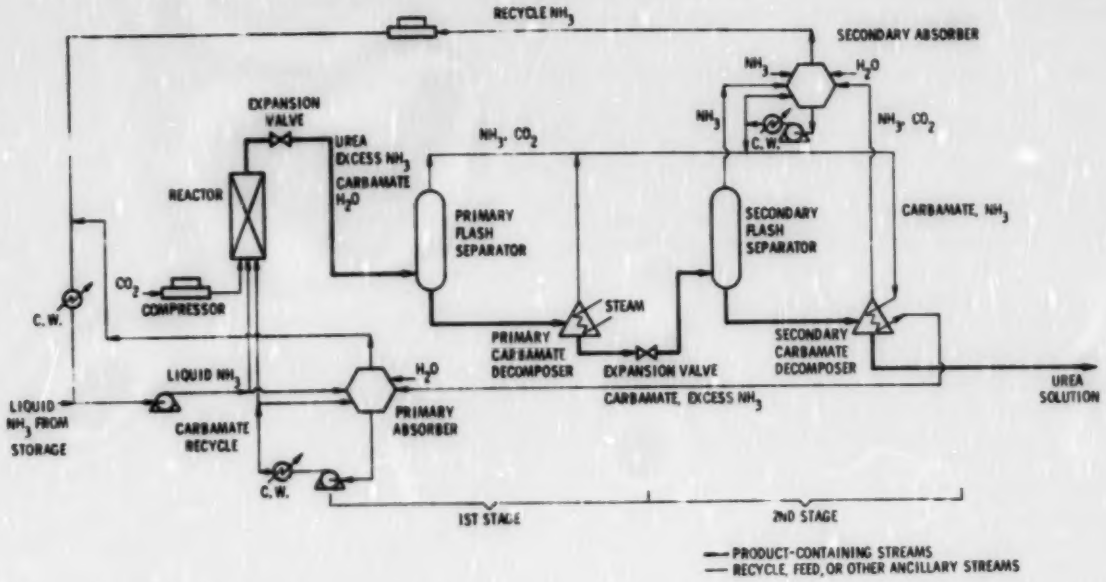

Figure 18. Chemico total recycle urea process.

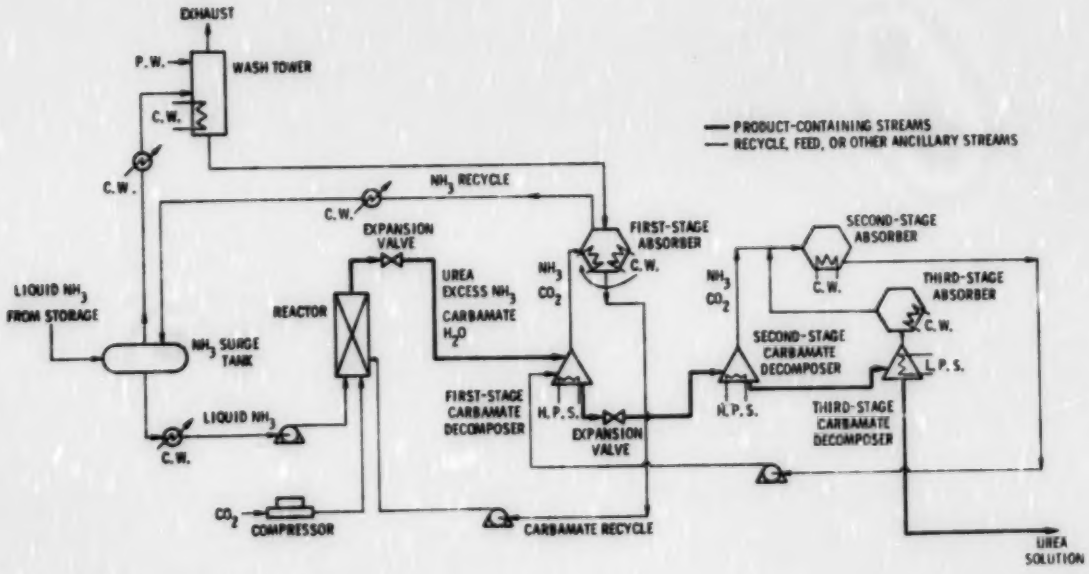

Figure 19. Lonza-Lummus urea process.

(4) Summary of total recycle processes--A summary of the basic operating parameters for the total recycle systems is given in Table 3 (1, 11-26).

Two facts must be considered when interpreting Table 3:

- Much process and design information is not available due to its proprietary nature.
- Some of the facilities have been designed by company personnel based on basic process technology; they do not use contractual packaged design and are not listed in Table 3.

TABLE 3. SUMMARY OF TOTAL RECYCLE SYSTEMS

Process	Molar feed ratio		Percent conversion to urea (per pass)			Reactor operating parameters		Reference
	NH_3/CO_2	H_2O/CO_2	NH_3	CO_2	Carbamate	Temp., °C	Pressure, MPa	
CPI-Allied	4 to 4.5/1	-[a]	-[a]	85	-[a]	194 to 233	30	12,13
Inventa gas recycle	2/1	-[a]	-[a]	50	-[a]	180 to 200	20	1,14,15
Stamicarbon CO_2 Stripping	2.4 to 2.9/1	-[a]	65 to 85	70 to 85	-[a]	170 to 190	12 to 15	11,13
Montecatini	3.5/1	0.6/1	-[a]	-[a]	-[a]	195	20	13,16,18
Pechiney	2/1	-[a]	-[a]	-[a]	40 to 50	177 to 183	20	14,15,17
Inventa liquid recycle	3.5 to 4.0/1	-[a]	-[a]	62 to 65	-[a]	185	23	11
Mitsui Toatsu[b]	4.3/1	-[a]	-[a]	67	-[a]	190	24	11,19,20
Stamicarbon total recycle	-[a]	-[a]	-[a]	-[a]	-[a]	170 to 190	20	11
SNAM PROGETTI NH_3 Stripping	3.3 to 3.5/1	-[a]	-[a]	60	-[a]	180 to 190	13 to 16 or 20 to 25	11,13,21 22,23,24
Chemico	4/1	-[a]	-[a]	64 to 70	-[a]	175 to 200	19 to 23	11,13,25
Lonza-Lummus	4.5/1	-[a]	-[a]	-[a]	70	200	30 to 34	11,26

[a] Information not available.

[b] Operating parameters for "D" Improved process only.

d. Emission Points from Solution Production--
Emissions from the solution production step in the urea manufacturing process arise from individual process exhausts and from leaking pump seals. A quick review of Figures 9 through 19 shows that the following processes have exhausts:

- Stamicarbon CO_2 Stripping
- Montecatini complete recycle
- Stamicarbon total recycle
- Lonza-Lummus

Pump seals are a normal item for preventive maintenance. If a seal starts to leak, the pump is shut down and the packing is replaced. Therefore pump seals will not be considered further. The only emission points to be discussed later will be process exhausts.

2. Solid Urea Production

Approximately 62% of the urea solution produced is converted to a solid product. This means that in 1975 2.14×10^6 metric tons of urea were produced in solid form. Figure 20 is a flowsheet of the entire urea solidification process. As can be seen, each section has a number of steps which will be discussed in subsequent sections.

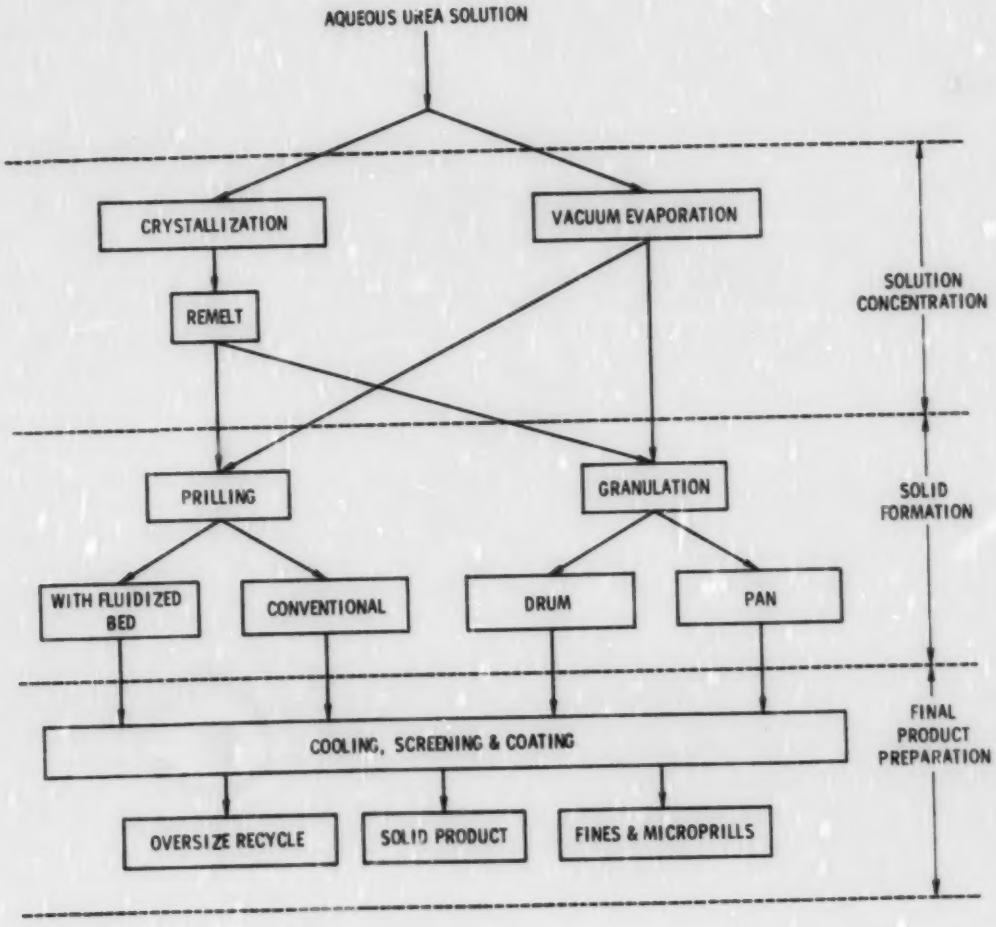

Figure 20. Solidification of urea.

The formation of solid urea requires a critical balance between temperature, retention time, and airflow due to several physical characteristics; namely, melting point, heat of crystallization, and decomposition properties. These factors lead to careful control and at times adaptation of established techniques depending upon the environment in which the material is produced.

a. Solution Concentration--
Solution concentration can be achieved by two methods as shown in Figure 20: vacuum evaporation and crystallization. Less than 25% of the urea solution made for solid production is concentrated by crystallization. This percentage is determined by calculating the percent of urea produced for consumption in plastics and other areas (10.1% and 4.8% of the total urea solution production) requiring an extremely low biuret content. Feed to the solution concentration section is 70% to 75% urea solution that already contains 0.3% to 0.7% biuret. Since crystallizers operate at 60°C, versus 120°C to 140°C for evaporators, they hold to a minimum any additional biuret formation (1, 10).

The percentage of urea production devoted to low-biuret uses is 14.9%; this is 24% of solid urea production. This approximation has been validated by industry sources who estimated the ratio of crystallizers to evaporators to be 1 to 3.

(1) Crystallization and dewatering--Urea crystallization as a solution concentration method was introduced in 1953 and has since grown in popularity. Currently both vacuum and atmospheric crystallizers are in use. A vacuum crystallizer operating at 8 kPa and 60°C (1) evaporates water using the sensible heat of the urea solution and the heat of crystallization. Additional heat can be supplied by pumping the urea solution through one of the decomposers where it is heated by exchange. The crystallizer slurry, containing about 30% (weight) urea crystals in suspension, is placed in a continuous-type pusher centrifuge where the crystals are separated, washed, and dried to less than 0.3% moisture. The dewatered crystals are melted and sprayed into the solidification device.

(2) Evaporation--A thin-film (falling-film type) evaporator operating at atmospheric pressure is most commonly used for evaporation. While a falling-film evaporator is standard, any type of thin-film evaporator in which the temperature can be controlled to between 120°C (inlet) and 140°C (outlet) can be employed. The Tennessee Valley Authority (TVA) used a small shell-and-tube preliminary evaporator followed by an eight-disc rotary disc falling-film forced evaporator in its pilot-scale

unit (27). The use of two evaporators in series is reported to be the trend in current plant constructions (10). This arrangement has proven most successful in producing the 98% to 99.5% urea solution necessary for solid formation.

b. Solid Formation--
The actual solid product can be formed by two methods, prilling and granulation, each of which has two possible modifications. Based on an estimated 351 days of production (365 minus 14 days planned maintenance shutdown), the daily production rate for the industry can be calculated from 1975 yearly production data to be 6,097 metric tons/day. Urea granulation by the Spherodizer® process (to be described later) has a daily capacity of 5,201 metric tons. Since Spherodizers are reported to operate at 100% capacity on an industry average (28), approximately 85% of the solid urea produced is estimated to be produced by the Spherodizer. Other granulation process productions are assumed to be negligible, leaving 15% of solid urea production that employs prilling for solid formation.

(1) Prilling--The basic methodology for prilling is well established. Concentrated urea solution is pumped to the top of a tower 30.5 m to 33.5 m high and forced through a spray device. Several types of devices, ranging from a single nozzle to multiple nozzles or a spinning bucket are used. The droplets thus formed fall countercurrent to a rising airstream which acts as a heat transfer agent that cools and solidifies the material.

The material may fall onto a fluidized bed which acts as a cooler or simply onto a belt conveyor which carries the material to storage. Table 4 is a comparison of the particle sizes found in different samples of prilled urea. Sample A was taken from a bin at a fertilizer bulk mixing facility (2). Sample B is from a urea plant facility and compares coated (1.2% to 2.0% clay) and uncoated urea prills (29). Sample C is an analysis of unscreened prilled product from a urea plant. Sample D is a size distribution of final product from a urea prilling facility. Size distributions of samples C and D were obtained from industry contacts. Table 5 presents some characteristics of urea prilling operations compiled from several literature sources and industry contacts.

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(27) Granular Urea and Ammonium Nitrate. Nitrogen, 95:31-36, May/June 1975.

(28) Personal communication with J. C. Reynolds, C & I/Girdler, Inc., Louisville, Kentucky, August 1977.

(29) Reed, R. M., and J. C. Reynolds. The Spherodizer Granulation Process. Chemical Engineering Progress, 69(2):62-66, 1973.

TABLE 4. SIZE DISTRIBUTION OF UREA PRILLED PRODUCT

Screen size		Percent retained on screens				
			Sample B			
mm	mesh	Sample A	Uncoated	Coated	Sample C	Sample D
3.4	6	-[a]	0	0	0	-[b]
2.4	8	-[a]	1	0	2.2	-[b]
1.7	10	-[a]	17	1	77.1	12
1.4	12	-[a]	-[b]	-[b]	15.2	39
1.2	14	-[a]	-[b]	-[b]	3.3	35
1.0	16	-[a]	78	94	1.1	8
0.8	20	-[a]	-[b]	-[b]	0.5	3
250 µm	60	-[a]	4[c]	5[c]	0.6[d]	3[e]
105 µm	150	0.0046	-[c]	-[c]	-[b]	-[e]
74 µm	200	0.0028	-[c]	-[c]	-[b]	-[e]
44 µm	325	0.0090	-[c]	-[c]	-[b]	-[e]
≤44 µm	≤325	0.0154	-[c]	-[c]	-[b]	-[e]

[a] >99% of sample retained on 250-µm (60-mesh) screen.

[b] No information available.

[c] Remainder as indicated is <1.0 mm (16 mesh).

[d] This quantity indicated as the pan quantity.

[e] Remainder is indicated as <0.8 mm (20 mesh).

TABLE 5. PRILL TOWER CHARACTERISTICS

Parameter	Value
Free fall height	30.5 m to 33.5 m
Tower cross section	circular or square
Cross section area	28 m^2 to 113 m^2
Spray temperature	135°C to 144°C
Prill exit temperature	~80°C

(2) Granulation--The basic principle of granulation involves spraying molten urea onto fine urea particles to increase the granule size in a layered fashion. This type of particle formation produces a stronger particle than does prilling. This stronger structure does not permit as much crushing in agricultural machinery, thereby resulting in a better material distribution on the field. As a result, a major market for solid urea produced by granulation is the fertilizer industry.

There are two basic designs of granulation equipment: pan and drum. These two processes are discussed in the following sections.

(a) Pan granulation--Figure 21 is a sketch of a pan granulator (30). This type of operation was first introduced for use with fertilizers in 1950, and the TVA began work on the process in 1963 (27). Powdery material is introduced at the top of a rotating, tilted pan and tumbles to the lowest point of rotation. As the granules are carried up by the rotating pan they are mixed into a deep bed of granules, where the lightest particles rise farthest before falling back through the spray to the lower side

(30) Young, R. D., and I. W. McCamy. TVA Development Work and Experience with Pan Granulation of Fertilizers. Canadian Journal of Chemical Engineering (Ottawa, Ontario), 45(2): 50-56, 1967.

and back into the bed. As the granules grow they are progressively displaced to the surface of the deep bed by the incoming smaller particles. Eventually the large granules tumble over the side of the pan.

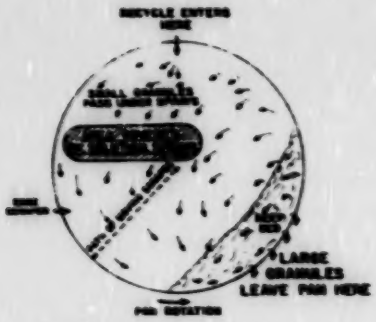

Figure 21. Sketch of pan granulator (30).

TVA has conducted pilot-plant studies in which the 98.5% to 99% urea solution from an evaporator was sprayed onto a bed of recycled fines at a temperature of 145°C. In this unit the pan was tilted 1.15 rad and rotated at 1.84 rad/s. The granules leaving the pan were at 99°C and went directly to a cooler. The screen analysis of the material leaving the granulator is shown in Table 6.

TABLE 6. SCREEN ANALYSIS OF PAN GRANULATOR PRODUCT

Screen size		Percent retained
mm	mesh	on screen
3.4	6	6
2.4	8	17
1.7	10	56
1.2	14	12
0.8	20	3
≤0.8	≤20	6

The granules leaving the pan were cooled in a conventional countercurrent rotary cooler and finally screened to the following size range by vibratory screens:

Screen size		Percent retained
mm	mesh	
2.4	8	71
1.7	10	29

The sized product was further cooled in another rotary unit and coated with approximately 0.7% (by weight) kaolin. A mixture of 90% light lubricating oil and 10% paraffin wax was sprayed as a dust suppressant in quantities of approximately 0.3% by weight (27).

Norsk Hydro has developed a pan granulation process that operates at a temperature close to the crystallization temperature of urea. While conventional systems operate approximately 40°C lower, the Norsk Hydro process temperature (with a maximum temperature difference of 25°C) claims a higher output because of increased crystal growth rate. The tamped bulk density of this product is 1,000 kg/m^3, as compared with a loose pour density for conventional pan-granulated material of 700 kg/m^3. At least 95% of this material is between 4 mm and 11 mm in diameter.

(b) Drum granulation--Figure 22 is a cross-sectional sketch of the Spherodizer®, a drum granulation unit designed by C&I/Girdler. There are currently at least 18 Spherodizer units in operation in the U.S. (see Table 7, having a total capacity of 5,201 metric tons/day, accounting for 85% of the domestic urea solid production (31).

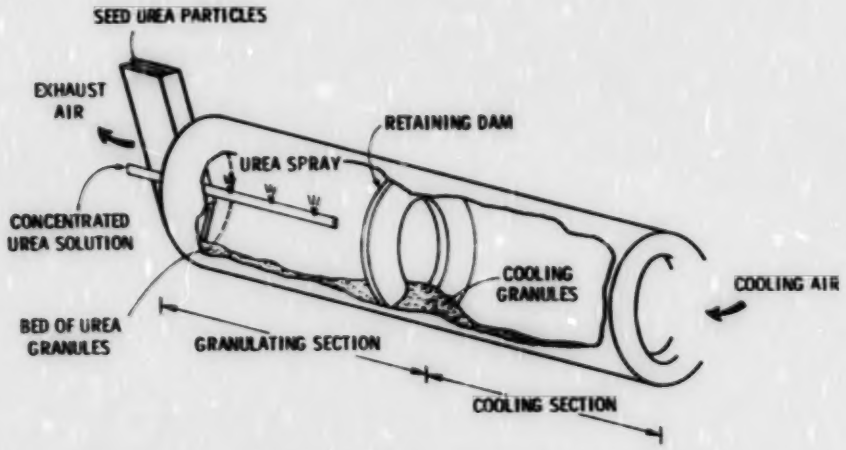

Figure 22. Cross section of Spherodizer.

(31) Reynolds, J. C. and R. M. Reed. Progress Report on SPHERODIZER Granulation 1975-76. In: Proceedings of The Fertilizer Institute Environmental Symposium (New Orleans, Louisiana), The Fertilizer Institute, Washington, D.C., pp. 193-215. 1976.

TABLE 7. U.S. SPHERODIZER UREA GRANULATION PLANTS (31)

Company name	Capacity, metric tons/day	No. of drums	Location
Agrico Chemical Co.	544	2	Donaldsonville, Louisiana
Agrico Chemical Co.	907	3	Blytheville, Arkansas
CF Industries, Inc.	907	3	Donaldsonville, Louisiana
CF Industries, Inc.	1,211	4	Donaldsonville, Louisiana
Collier Carbon and Chemical Co.	1,088	4	Kenai, Alaska
Cooperative Farm Chemical Association	544	2	Lawrence, Kansas
TOTAL	5,201	18	
Average size 289 metric tons/day			

The drums are approximately 4.3 m in diameter with an average capacity of 289 metric tons/day. Other parameters such as length of drum and rotation speed vary at each installation. Fine urea particulates enter the granulating section at a recycle ratio (recycle:product) of 2:1. The granulating section of the drum is separated from the cooling section by a dam, the height of which regulates the particle residence time in the granulating section. This granulating section is also equipped with lifting flights (see Figure 23) which pick up the particle material and drop it from the top of the drum, creating a falling curtain of seed material. The seed material is undersized product recycled to the drum.

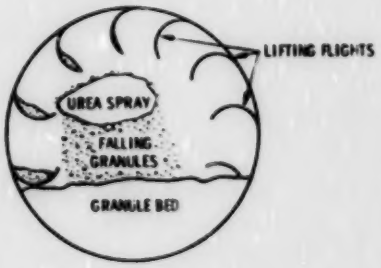

Figure 23. Spherodizer drum - end view.

Urea melt at 138°C and 99.3% urea comes through the spray bar onto the falling curtain and tumbling bed of particles (see Figures 22 and 23). This application technique ensures that the particles will be coated with thin, uniform layers. Solidification is facilitated by passing a stream of air countercurrent to the product flow. The air enters the cooling section at approximately 10°C and exits the granulating section at 77°C to 88°C.

The product leaves the drum at 43°C and contains 0.06% water. The material is then sized, with the oversized and undersized particles being recycled through a crusher to the entrance of the drum. The product is coated (27) with 1.2% to 2.0% clay (based on final weight).

Urea granules produced by this process have a crushing strength 1.8 to 2.8 times that of urea prills. The bulk density is 700 kg/m^3 for loose pour and 800 kg/m^3 for tamped product. Table 8 shows the size distribution of screened urea product and the differences which can exist between two processes using different screen size ranges for final product sorting.

TABLE 8. SIZE DISTRIBUTION OF SCREENED UREA PRODUCT FROM A SPHERODIZER UNIT (27)

Screen size		Percent retained on screen	
mm	mesh	Sample A[a]	Sample B[b]
3.4	6	1.5	2.7
2.4	8	89.6	80.1
1.7	10	8.8	17.1
1.2	14	0.1	0.1

[a]Product from process which screens to eliminate any granules larger than 3.4 mm (6 mesh) and smaller than 2.4 mm (8 mesh).

[b]Product from process which screens to eliminate any granules larger than 3.4 mm (6 mesh) and smaller than 2.0 mm (9 mesh).

c. Final Product Preparation--
Final product preparation consists of cooling, screening, and coating.

(1) Cooling--Less than 5% of the urea industry uses auxiliary coolers to lower the temperature of the solid particles between the solid formation and screening, shipment or storage operations. There are at least two processes in which a cooling stage is an integral part of the solid formation process-drum granulation and fluidized bed prilling. In the other processes, the particles fall directly onto a conveyor belt which carries them to either a screen or storage.

(2) Screening--The product can be screened by inclined vibrating screens immediately after solid particle production, before shipment, or both. The oversized material is recycled to the

process after it is either crushed and remelted or dissolved in solution. The fines are recycled to the process as seed material, redissolved, or used as a product when needed for mixing with livestock feed. The product is stored for bagging or bulk shipment.

(3) Coating--Less than 10% of the solid urea produced is coated because the practice of injecting formaldehyde or phosphate-based additives into the melt prior to solid formation has increased. The structures and quantities of the phosphate-based additives are proprietary. The quantities of formaldehyde used are also proprietary; however, quantities well below 0.1 wt % are used. These additives do not alter the chemical characteristics of the final particle and therefore leave it more compatible with product application (e.g., feed material for urea-formaldehyde resins) than coated particles.

When coating occurs, diatomaceous earth or kaolin is added to the particles in quantities of 0.3 wt% to 2.0 wt%. Another coating which has been used is a light oil-paraffin mixture that acts as a dust suppressant in the TVA pan granulation process. This coating process, like sizing, occurs inside a large warehouse and requires no external vents.

d. Emission Points from Solid Production--
Potential emission points and the species emitted are listed:

Emission point	Species
Evaporator	Ammonia, particulate
Crystallizer	Ammonia
Crystallizer centrifuge	Ammonia
Prilling tower	Ammonia, particulate
Granulator	Ammonia, particulate

Emissions from all of these points will not occur at any one plant. For example, no plant utilizes both an evaporator and a crystallizer, or a prilling tower and a granulator.

3. Product Shipment

a. Shipment of Bulk Solutions--
Approximately 38% of all urea is sold as a solution and shipped in bulk by railroad tank cars or tank trucks. These tank cars can be loaded directly from the process or from storage tanks. At least one company has a pipeline for deliverying urea solutions.

Bulk solution loading, like bulk loading of solid urea, takes place under cover of a two-sided shed. A delivery tube is placed inside the manhole on the top of the trailer, approximately 3.7 m off the ground. The liquid urea solution, approximately 70% urea, is pumped into the tank car at 66°C and maintained at that temperature because the cars are double insulated.

b. Storage, Packaging, and Bulk Loading of Solids--
Solid urea can be stored, bagged, or shipped in bulk. Storage facilities are large warehouses where the urea is put in piles 9 m to 12 m high and at least 23 m in base diameter via an overhead conveyor system.

The stored urea is either bagged or bulk loaded for shipment from this stockpile. Material to be shipped in bulk is screened and carried to an overhead conveyor for disbursement. The conveyor drops the material into a bulk hopper train car or bulk truck at a height of 3.7 m. This operation is done under cover of a shed to prevent moisture contamination of the urea. In a few cases, plants near major waterways have shipped solid product by barge.

Urea may also be shipped in bags (1). Domestic shipments are made in 4-ply, polyethylene-coated, 20 4-kg paper bags. Exporting is done in 6-ply, polyethylene-coated, 36.3-kg paper bags. This operation is done in a large warehouse using one of many types of automatic bagging machines.

D. EMISSIONS FROM PRODUCT SHIPMENT

In the bulk loading of solution product, air contained in the empty space of the railroad tank car or tank truck is displaced by the liquid and emitted to the atmosphere. This displaced air contains ammonia.

Emissions from shipment of solid product consist of small urea particles that are entrained into the air during the operation.

SECTION IV

EMISSIONS

A. SELECTED EMISSIONS

As discussed previously, urea is formed by dehydrating the ammonium carbamate which is produced when ammonia is reacted with carbon dioxide. This urea may be sold as an aqueous solution or solidified to form a solid product. The manufacturing process causes two types of emissions, ammonia and particulates. Both materials are emitted during the solidification process, but only ammonia is released from the solution formation process.

Particulate emissions are composed primarily (>99%) of urea, except for those particulate emissions released from the coating operation; these particulates consist of coating materials. Although no analyses are available, possible impurities such as biuret have lower vapor pressures than urea itself and therefore would not be present in the particulate emissions at concentrations higher than in the bulk product. Formaldehyde added to urea reacts to form monomethylurea and so is not present as the pure compound, which does have a higher vapor pressure than urea.

Since urea is normally used as a fertilizer and animal feed, it is not considered a hazardous material; no threshold limit value (TLV) has been assigned to it (32). Biuret is always present as an impurity, but its concentration is controlled to less than 0.5% in fertilizer-grade product. Although biuret is toxic to plants, it is not hazardous to animals; no TLV has been assigned to it. Other possible impurities include triuret, cyanuric acid, and ammelide (1). Cyanuric acid is a hazardous compound, but an analysis of urea shows that biuret is the main impurity (present at concentrations between 1% and 0.1%), with other impurities present at less than 0.1% (1).

Coating materials applied to urea may be clays, diatomaceous earths, or a paraffin/oil mixture. Diatomaceous earth has been

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(32) TLVs® Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1976. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1976. 94 pp.

assigned a TLV of 1.5 mg/m^3 (respirable dust, <5 μm); kaolin clay has a TLV of 10 mg/m^3 (32).

Proprietary phosphate-based additives are not believed to be hazardous since phosphate compounds in general are not toxic. Formaldehyde, also used as an additive, has been assigned a TLV of 3 mg/m^3 (32). However, it reacts with urea to form monomethyl urea and higher derivatives that do not have established TLV's.

Possible trace element contamination was not studied. Since the raw materials for urea synthesis are carbon dioxide and ammonia (i.e., gaseous species), the only source of trace elements would be from equipment corrosion (ammonium carbamate solution is highly corrosive). If a urea plant manufacturing 100,000 metric tons/yr had trace metals present in the final product at a concentration of one part per billion (1 ppb), the annual metal loss due to corrosion would be 100 g. A concentration of one part per million would correspond to a corrosion loss of 100 kg/yr. Equipment failure would soon result from losses of 100 kg/yr, and it is therefore concluded that any trace metal impurities must be present at levels below 1 ppm. By way of confirmation the product specifications for fertilizer-grade urea include a maximum iron concentration of 2 ppm (1).

In the subsequent discussion in this section, emissions are classified as either particulates or ammonia. Potential environmental affects are evaluated based on the primary ambient air quality standard for particulates of 260 μg/m^3 and the TLV for ammonia of 18 mg/m^3.

B. EMISSION FACTORS

Ammonia and particulates emitted per unit of product produced for each process step in urea manufacture are discussed below based on engineering estimates, information from industrial sources, and data from the open literature.

1. Solution Production

The emissions from the solution production step in urea manufacturing come from individual process exhaust vents and fugitive sources. The fugitive emissions are due to evaporation from spills and leakage in pump seals, valves, and compressors. Ammonia is the only emission species since only gaseous emissions are released.

As has been noted in Section III.C, solution production processes utilized by the industry generally do not have process exhaust vents to the atmosphere, except for the following four processes: Stamicarbon CO_2 stripping process, Montecatini complete recycle process, Stamicarbon total recycle process, and Lonza-Lummus process. In the above total recycle processes, unreacted

ammonia from the reactor and ammonia generated from the carbamate decomposer are removed from the gas stream by various absorbers for recycling back to the reactor. Tests on the gas stream vented to the atmosphere indicate that there is no detectable ammonia in this stream (12).

Data are not available to quantify fugitive emissions from the solution production step. It was assumed that these emissions are negligible for the following reasons

- OSHA[a] regulations limit the allowable ammonia concentration in the work place.
- The odor of ammonia from leaks is easily detected.
- Maintenance of pump seals, valves, and compressors is regularly performed to avoid product loss and to preserve a healthy working environment.

Based on the above discussion, no emission factor was derived for emissions from the solution production step.

2. Solution Concentration

a. Evaporation--
Evaporation is used in over 75% of the solid production processes as a method of solution concentration. More than 90% of the facilities using evaporation use a thin-film evaporator operating at atmospheric pressure. Air passes countercurrent to the falling film of urea solution, releasing ammonia as well as particulates. Very few (<5%) of the plants allow this stream to exhaust to the atmosphere. In some cases (approximately 50%), the off-gas from the evaporator passes through a condenser, and the condensate is either sewered (where allowed by water quality standards) or sold as a dilute fertilizer solution. In the remainder of the installations, the evaporator off-gas is scrubbed to recover valuable ammonia and urea. Types of scrubbers used in this application as well as those used in granulation are discussed in Section V.

A number of factors affect the ammonia emission rate from evaporators. A partial list includes:

- residual ammonia in feed stream, i.e., from solution production process
- biuret concentration
- amount of urea hydrolysis
- control efficiency of scrubber or condenser used

[a]Occupational Health and Safety Administration.

The level of residual ammonia in the feed stream to the evaporator is one of the most significant factors, resulting in a possible range in ammonia concentration from a few hundred parts per million to as much as 0.5%. A material balance calculation shows that, in the absence of controls, this will correspond to an ammonia emission factor of 0.4 g to 7 g per kg of product.

Testing has been conducted by one firm which employs wet scrubbers to recover urea and ammonia (33). The data resulting from these tests showed that 1.73 ± 64%[a] grams of ammonia and 0.107 ± 28% grams of particulate per kilogram of product (95% confidence) were emitted from the scrubber. The above values for ammonia and particulate emissions thus represent controlled emission factors. The test data also indicate an uncontrolled emission factor of 8.55 g/kg of product for particulates. Scrubber efficiencies are therefore on the order of 99% for particulates, but at most 75% for ammonia. The scrubbing efficiency for ammonia could probably be improved by using an acidic scrubbing solution.

b. Crystallization, Dewatering, and Remelting--
A wide variety of crystallizers are used in those processes employing crystallization as a solution concentration process (approximately 25% of solution concentration capacity). The emission characteristics and quantitites, being dependent upon the particular equipment type, vary from plant to plant. In most cases, however, any exhaust from the crystallizer passes through a condenser and the condensate is sewered.

The slurry from the crystallizer, containing approximately 30% crystals, is placed in a continuous centrifuge where the crystals are dewatered to <0.3% water. While dryers are occasionally used, centrifugation is used in more than 95% of those processes using crystallization. After dewatering, the crystals are melted for use in the subsequent solid formation processes.

Emissions from these operations are expected to be less than those from evaporation. No airstream passes through the vessels to entrain particulates and remove residual ammonia from solution.

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[a]Emission factors are given with their corresponding uncertainty based on a Student t test of the available data.

(33) Sanders, L. Monitoring and Control of Gaseous and Particulate Emission from Fertilizer Complex. Paper No. 75-5.6, presented at 69th Annual Meeting of the Air Pollution Control Association, Portland, Oregon, June 27-July 1, 1976. 14 pp.

Operating temperatures are also lower. Although some ammonia may escape from exhaust vents, the rest will remain in the aqueous phase that leaves the centrifuge. There are no data available to quantify emissions from these processes. For worst case evaluation purposes it was assumed that the emission factors developed for evaporation are also applicable to this emission source. In subsequent calculations, only one set of emission factors is used for emissions from the solution concentration process.

3. Prilling

As discussed previously, 15% of solid urea is manufactured by prilling--droplets of urea melt falling countercurrent to a cooling airstream in which they cool and solidify. Ammonia and particulate emissions result from this operation. The ammonia is released from the possible degradation of urea to biuret and also from excess ammonia still present in the spraying stream. The particulates are small urea droplets formed during spraying which solidify and leave the tower in the exiting gas stream rather than falling to the bottom.

Table 9 shows data for ammonia and particulate emissions from the prill towers of three plants that have conducted testing. The ammonia data were averaged to give an emission factor of 0.40 g/kg ± 84%. For particulates, another averaging procedure was used to obtain the average emission from a collection of average values, since the original emissions data were not available. The following equations are derived in Appendix B:

$$\bar{x}_T = \frac{\sum_{i=1}^{m} n_i \bar{x}_i}{\sum_{i=1}^{m} n_i} \tag{7}$$

and

$$s_T = \left[\frac{\sum_{i=1}^{m} (n_i - 1) s_i^2 + \sum_{i=1}^{m} n_i \bar{x}_i^2 - \bar{x}_T^2 \sum_{i=1}^{m} n_i}{\left(\sum_{i=1}^{m} n_i \right) - 1} \right]^{1/2} \tag{8}$$

where $\bar{x}_T$ = average of the averages from each sample
n_i = number of test points in the i-th sample
$\bar{x}_i$ = average of test points in the i-th sample
m = total number of samples

s_T = standard deviation of $\bar{x}_T$

s_i = standard deviation of $\bar{x}_i$ for the i-th sample

TABLE 9. EMISSION DATA FOR PRILLING TOWER FROM SOURCE TESTS AT THREE UNCONTROLLED UREA PLANTS

Parameter	Plant number 1	2	3	Average
Actual particulate emission factor, g/kg	1.55 ± 6.2%	1.6 ± 172%[a]	1.85 ± 12.8%	3.2 ± 17%[b]
Number of samples for particulates	30	3[a]	6	NA[c]
Ammonia concentration, ppm	30	25 to 30	30	28.8[d]
Airflow rate, m^3/s	35.4	42.5 to 47.2	141.6	66.7[d]
Actual ammonia emission rate,[e] g/s	0.82	0.82 to 1.09	3.28	1.5[d]
Prill tower capacity, kg urea/s	2.1	3.7	4.7	3.5
Actual ammonia emission factor,[e] g/kg	0.39	0.22 to 0.29	0.70	0.40[d]

[a]Each of these three samples was the average value of several tests at different operating parameters. It was assumed that these variations in operating parameters do not exceed the variations experienced in normal operation.

[b]Determined using Equations 7 and 8.

[c]Not applicable.

[d]Average determined by averaging extremes of plant 2 with others single values.

[e]These numbers are actual, not representative, since they are based on actual, not representative, source measurements and plant capacity.

The average emission factors presented in Table 9 were used for the subsequent calculations. However, emission rates can fluctuate widely with changes in such variables as:

- type of spraying device used
- air velocity
- spray temperature
- type of product made

Additional factors that affect prilling emissions can be found in the literature (33).

4. Granulation

The Spherodizer granulation process is used by four companies in the U.S. to produce approximately 85% of the solid urea manufactured. Scrubbers are standard equipment on granulators, since up to 20% of the product may be entrained in the cooling

air stream (34). Therefore, the scurbber will be considered as the emission point for the granulator.

Tests conducted by C & I/Girdler, Inc., show that scrubbers have an average particulate removal efficiency of 99.9% (31). The same test give an emission factor from the scrubbers of 0.20 ± 25% grams of particulate per kilogram urea produced (95% confidence level). Other tests have given a particulate emission factor of 0.084 ± 29% g/kg urea and ammonia emissions of 0.25 ± 48% g/kg urea (95% confidence level) (33).

The different emission factors for particulates are a consequence of different scrubber efficiencies. In subsequent sections both values are used to give a range of possible emission factors.

5. Solid Product Finishing

This section includes any cooling, screening, or coating operations which may take place in the final preparation of the solid urea product. Less than 5% of the industry uses an auxiliary cooling step in final solid preparation. In at least two processes, drum granulation and fluidized-bed prilling, the cooling stage is an integral part of the solid formation, and any material entrained in the cooling air will exit from the solidification device. In other processes, the product falls directly on a conveyor belt which transports it to either screening or storage.

Solid product is screened (inside a building) before storage, before shipment, or both. The latter is most likely if a rigid particle size requirement is to be met. Emissions from this building due only to screening cannot be quantified. Often the same building houses storage and bagging facilities. Emissions from bagging operations are estimated, together with those from bulk loading of solid product, in the following subsection. That estimate is based on the amount of small urea particles in the prilled product that could be entrained in the air. The possible emissions of particulates from screening are covered in that total estimate, and further individual consideration is not given to emissions from the screening operation.

Less than 10% of the final product is coated, primarily due to the increased use of various additives in the melt. When coating occurs, diatomaceous earth or kaolin is added to the solid particles in quantities of up to 2.0 wt%. If the coating material is applied at a rate of 2 wt% and if 10% of this

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(34) Bress, D. F., and R. K. Fidler. New Concepts in Design of Urea Plants. Paper No. 13C, presented at 74th National Meeting of American Institute of Chemical Engineers, New Orleans, Louisiana, March 12-15, 1973. 22 pp.

material is released to the atmosphere (a worst case estimate), the emission factor for particulate emissions from this operation will be 2 g/kg of solid urea coated.

6. Solution Product Bulk Loading

In the bulk loading of solution product, liquid is pumped into a tank car or tank truck under cover of a shed. During the loading operation, the liquid filling the tank displaces air which contains ammonia vapor from entering urea solution.

Emission data are not available for this source; however, the ammonia emission factor can be estimated by considering the properties of 70% urea solution. Figure 24 is a diagram of the vapor pressure and specific gravity of urea solutions in water (8). The vapor pressure is assumed to be from ammonia rather than urea vapor. At a solution temperature of 339°K (66°C), the equilibrium vapor pressure of a 70% urea solution is 16.2 kPa. The total number of moles of ammonia contained in a specified volume, under equilibrium conditions, can be calculated from the ideal-gas law:

$$n = \frac{pV}{RT} \qquad (9)$$

where n = number of moles
p = vapor pressure, Pa
V = volume, m^3
R = 8.3 (Pa)(m^3)/(g/mole)(K)
T = temperature, °K

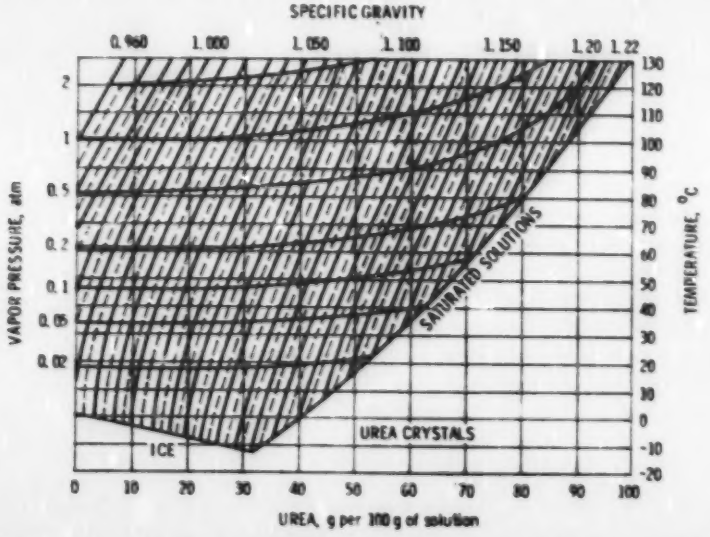

Figure 24. Vapor pressure and specific gravity of urea solutions in water (8).

In this case, V is the volume displaced by a 70% urea solution. The resultant emission factor for ammonia can be calculated as

$$E = \frac{nM}{Vd} = \frac{\frac{pV}{RT} \cdot M}{Vd} = \frac{PM}{RTd} \qquad (10)$$

where M = molecular weight of ammonia, g/mole
d = density of the 70% urea solution

Based on equilibrium vapor pressure (16.2 kPa), the temperature (339 K), the solution density (1.175 Mg/m^3, from specific gravity in Figure 24), and molecular weight (17 g/mole), the emission factor was calculated to be 0.083 g/kg of solution product loaded. Correcting for a 100% urea basis, the emission factor becomes 0.12 g/kg of 100% urea loaded.

7. Solid Product Bagging and Loading

Particulates are emitted from bagging for shipment and from the bulk loading of the solid urea product into railroad cars or barges. Data are not available to quantify the particulate emissions from this operation. A worst case estimate was made based on the particle size distribution given in Table 4. According to the Table, 0.0154% of the prilled urea product is ≤44 μm in size. Assuming that all of these small-size particles are air-entrained during the bagging and loading operations, the particulate emission factor becomes 0.15 g/kg of solid product loaded. It should be noted that this emission factor represents a worst case condition; the actual emission factor would be smaller than this. It is assumed that the proportion of fines (≤44-μm size particles) in granular solids is similar to that in prilled solids.

8. Summary of Emission Factors

The emission factors for ammonia and particulates, emitted from urea manufacture and discussed in the preceding subsections, are further summarized in Table 10 for each emitting operation. Solution production is not included in this table due to its insignificant emissions, as noted in Section IV.B.1. All the emission factors are based on the amount of pollutant emitted per unit of 100% urea product.

C. ENVIRONMENTAL EFFECTS

Air emission released during the production of urea are dispersed through the environment. This section examines the possible effects of these emissions and evaluates their severity.

TABLE 10. SUMMARY OF EMISSION FACTORS FOR UREA PRODUCTION[a,b]

Emitting operation	Emission factor, g/kg	
	Ammonia	Particulates
Solution concentration (controlled)	1.73 ± 64%	0.107 ± 28%
Prilling (uncontrolled)	0.40 ± 84%	3.2 ± 17%
Granulation	0.25 ± 48%	0.085 ± 29% to 0.20 ± 25%
Solid product finishing		2
Solution product bulk loading	0.12	
Solid product bagging and loading		0.15

[a] Blanks indicate no emissions from the operation.

[b] Percentages represent 95% confidence interval based on student t test.

1. Average Plant Characteristics

For evaluation purposes, the urea industry can be described in terms of certain average or predominant characteristics. These characteristics based on a generalized description of process variables gleaned from careful literature searches and conversations with industry representatives. They are averages of actual plant characteristics.

The following plant statistics have been derived from data presented in Appendix A, Table A-1:

- average plant capacity: 117,900 metric tons/yr
- average plant production rate: 69,000 metric tons/yr
- average county population density: 100 persons/km^2

The average plant capacity per day was determined to be 335.9 metric tons, based on 351 days/yr operation at full capacity. This value was used as a measure of the average maximum production rate, since most plants operate at full capacity sometime during the course of a year. The product distribution in the industry is 38% solution, 53% granulated solids, and 9% prilled solids. However, no single plant makes this distribution of products, and plants that make both solution and solids do not generally manufacture them simultaneously. Some production time is devoted to solutions, some to solids. Consequently, the

average maximum production rate for each process step was also assumed to be 335.9 metric tons/day.

In over 75% of the plants, evaporators are used to concentrate the solution prior to solid formation. In the remaining plants a crystallizer concentrates the solution.

Prill towers are circular with diameters of 6.1 m to 10.7 m and tower exit gas velocities of 1.22 m/s to 1.83 m/s. Tower heights range from 30.5 m to 33.5 m. Urea solution enters the towers at 132°C to 144°C, and the solid prills leave at 66°C to 83°C. The spray devices used may have a single-nozzle, multiple-nozzle, or Tuttle bucket. In over 90% of all prilling facilities, formaldehyde or a phosphate-based additive is placed in the urea solution before spraying.

Plants using a granulator for solid production use a drum granulator (Spherodizer). The drum is approximately 4.3 m in diameter and has a capacity of 289 metric tons/day. The urea is sprayed into the drum at 138°C, and solid granules leave at 43°C. As in prilling, additives are used to improve product characteristics.

Finishing operations include cooling, screening, and coating. Cooling as a distinct final step takes place in less than 5% of the industry. In the remaining cases, it is an integral part of the solid formation step, as it takes place at ambient conditions as the material is being transported on a conveyor belt. Screening can be done before storage, before shipment, or both. If the particular product market has strict product specifications, the latter case is most likely. Coating, which is applied to less than 10% of all solid final product, is not commonly used, primarily because of the increased use of formaldehyde or phosphate-based proprietary additives.

Solution and solid product are shipped in railroad tank cars and tank trucks. A few plants located near major waterways ship solid product by barge. Also at least one company has a pipeline for delivery of urea solutions.

Emission heights for the different process steps are as follows:

Evaporator	15.2 m
Prilling tower	30.5 m
Granulator	15.2 m
Coating, finishing, product finishing	ground level

2. Source Severity

One measure of the potential hazard of emissions from a source is given by the source severity, S, defined as:

$$S = \frac{\bar{\chi}_{max}}{F}$$

where $\bar{\chi}_{max}$ is the time-averaged maximum ground level concentration of each pollutant emitted from a process operation, and F is the primary ambient air quality standard for criteria pollutants (particulates in this case), or a reduced threshold limit value (TLV) for noncriteria pollutants:

$$F \equiv TLV \cdot 8/24 \cdot 0.01, \ g/m^3$$

The factor 8/24 adjusts the TLV for continuous rather than workday exposure, and the safety factor of 0.01 accounts for the fact that the general population is a higher risk group than healthy workers.

The value of $\bar{\chi}_{max}$ is the 24-hour average maximum ground level concentration for each emission species determined by the following equation (3, 35):

$$\bar{\chi}_{max} = \frac{2\,Q}{\pi e \bar{u} h^2} \left(\frac{t_o}{t}\right)^{0.17} \qquad (11)$$

where Q = emission rate, g/s
π = 3.14
e = 2.72
$\bar{u}$ = average wind speed, m/s
h = stack height, m
t_o = short term averaging time, 3 min
t = averaging time, 1,440 min (24 hr)

For ammonia and particulates, Equation 11 gives the following (3):

$$\bar{\chi}_{max} = \frac{0.0182\,Q}{h^2} \qquad (12)$$

Accordingly, the source severities for ammonia and particulates are:

$$S_{Ammonia} = \frac{303\,Q}{h^2} \quad \text{(TLV for ammonia: 18 mg/m}^3\text{)} \qquad (13)$$

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(35) Turner, D. B. Workbook of Atmospheric Dispersion Estimates. Public Health Service Publication No. 999-AP-26, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, May 1970. 84 pp.

$$S_{Particulates} = \frac{70\ Q}{h^2} \quad \text{(AAQS for particulates: 260 } \mu g/m^3\text{)} \quad (14)$$

The following equations have also been derived for ground level emissions of pollutants from a confined area such as emissions from the windows and doors of a building in which an operation is taking place (3):

$$\bar{X} = 1.048\ QD^{-1.814} \quad \text{(particulate or ammonia)} \quad (15)$$

$$S = 17{,}467\ QD^{-1.814} \quad \text{(ammonia only)} \quad (16)$$

$$S = 4{,}031\ QD^{-1.814} \quad \text{(particulates only)} \quad (17)$$

where D is the downwind distance from the emission point. In this case $\bar{X}$ is the average ground level concentration at the distance D. The highest concentration to which the general population is exposed occurs when D equals the distance from the emission point to the plant boundary. For the average urea plant this distance is estimated to be ∿400 m.

Table 11 summarizes values of $\bar{X}_{max}$ and S for the evaporator, prill tower, and granulator, based on an operating rate of 335.9 metric tons of urea/day. Severities exceed 1.0 for ammonia emissions from the evaporator and granulator. This indicates that the estimated average maximum ground level concentration for a representative plant is greater than the reduced TLV. The actual emission rates are highest for ammonia emissions from the evaporator and particulate emissions from the prill tower.

TABLE 11. EMISSION RATES, MAXIMUM GROUND LEVEL CONCENTRATIONS, AND SOURCE SEVERITIES FOR PROCESS OPERATIONS[a]

Emission point	Emission species	Emission rate, g/s	$\bar{X}_{max}$, $\mu g/m^3$	Source severity
Evaporator	Ammonia	6.73	530	8.82
	Particulate	0.392	30.8	0.12
Prill tower	Ammonia	1.56	30.4	0.51
	Particulate	12.44	243	0.94
Granulator	Ammonia	0.972	76.6	1.27
	Particulate	0.327 to 0.778	25.7 to 61.2	0.099 to 0.24

[a]Emissions from evaporation and granulation are controlled; emissions from prilling are uncontrolled, corresponding to current industry practice.

Maximum severities for ground level operations can be determined by plotting S versus D, using the appropriate emission rate for each process. This is done in Figure 25 for fugitive ammonia emissions from the bulk loading of urea solutions and in Figure 26 for particulate emissions from the bulk loading of solids. In each case, the severity falls below 1.0 well within the average plant boundary (D = 400 m). For fugitive ammonia emissions, S = 0.15 at the plant boundary; for fugitive particulate emissions, S = 0.045. Fugitive emissions from coating operations are not evaluated because: 1) coating takes place during less than 10% of urea production, and 2) the coating rate at an average plant is not known.

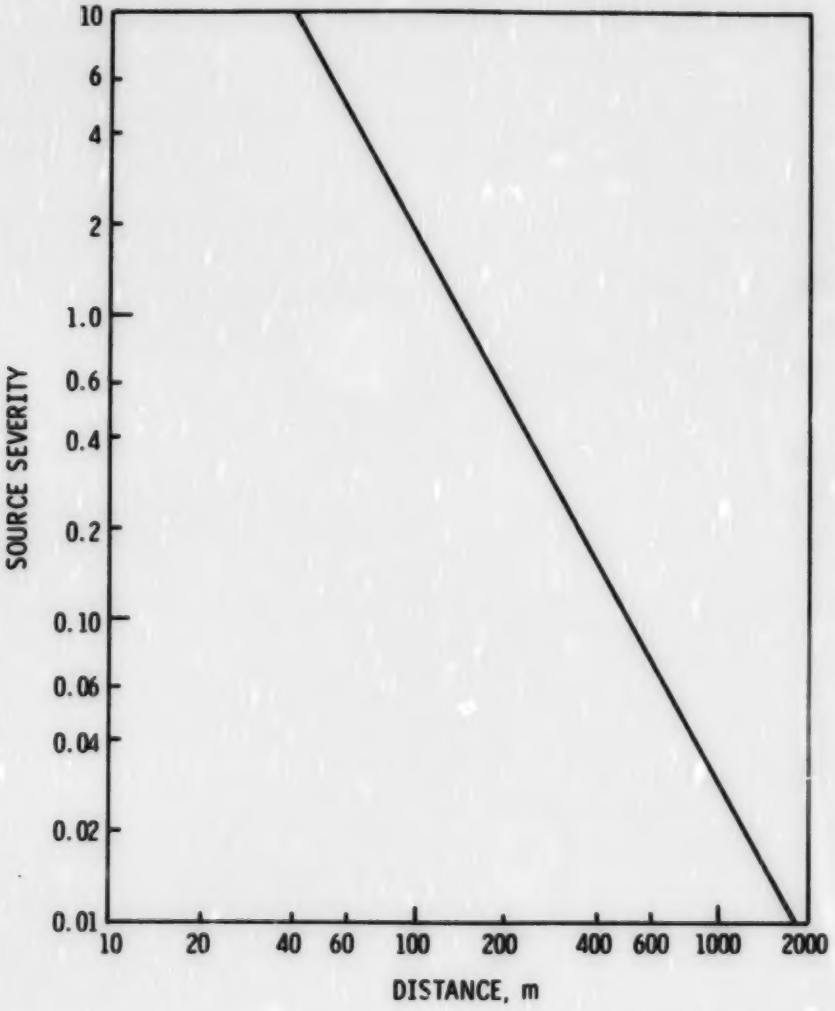

Figure 25. Source severity for fugitive ammonia emissions from the bulk loading of urea solutions.

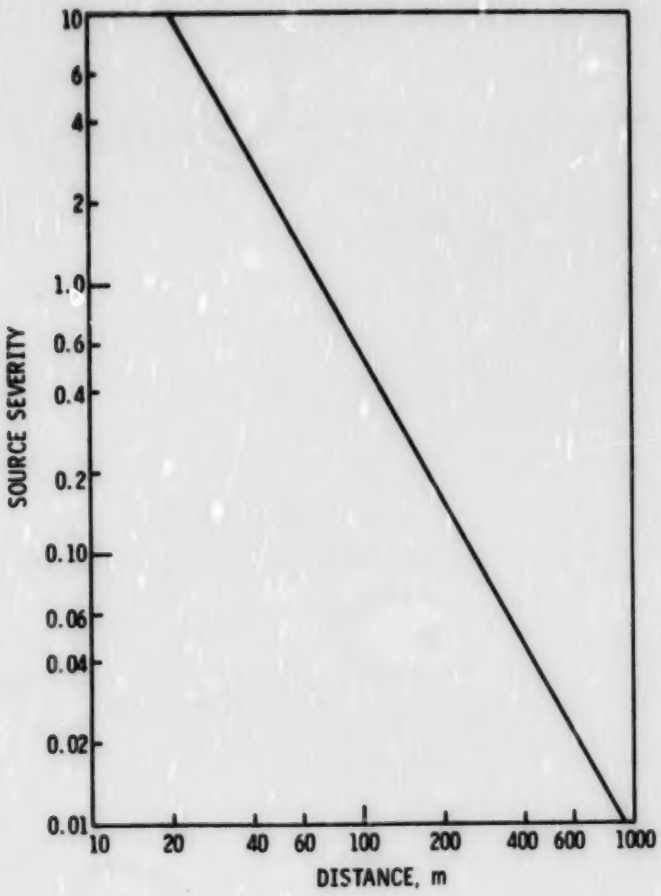

Figure 26. Source severity for fugitive particulate emissions from the bulk loading of urea solids.

In addition to the single value emission parameters presented in Table 11, it is desirable to determine the distribution of source severities by plant size across the industry. Figures 27-31 show these distributions for ammonia and particulate emissions from the evaporator, prill tower, and granulator. Severity distributions were calculated in the same way as the severities for average processes, using the individual plant capacities from Appendix A. An average emissions factor of 0.142 g/kg was used for particulate emissions from the granulator.

Severities do not exceed 1.0 for particulate emissions from the evaporator and granulator (these emissions are controlled by scrubbers). Severities exceed 1.0 for other emissions in the following proportions:

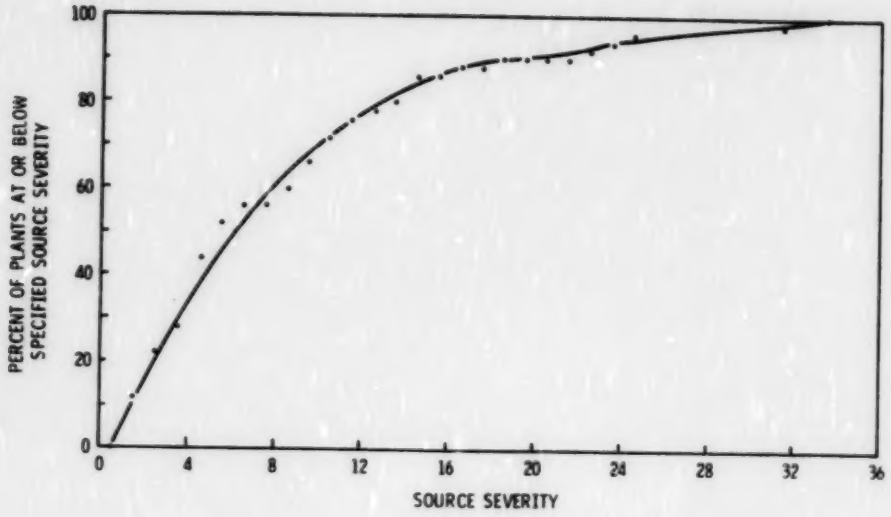

Figure 27. Source severity distribution for ammonia emissions from the evaporator.

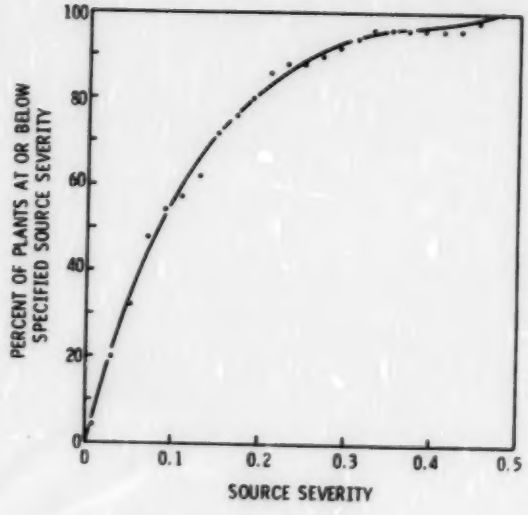

Figure 28. Source severity distribution for particulate emissions from the evaporator.

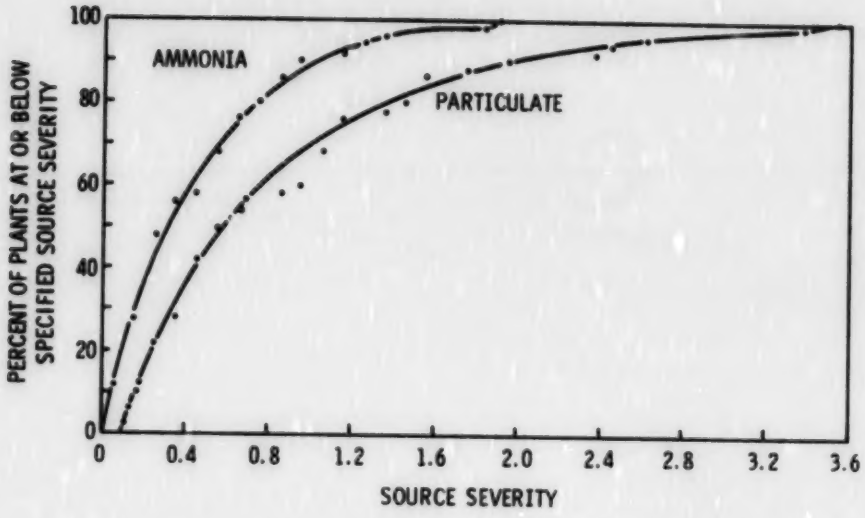

Figure 29. Source severity distribution for ammonia and particulate emissions from the prilling tower.

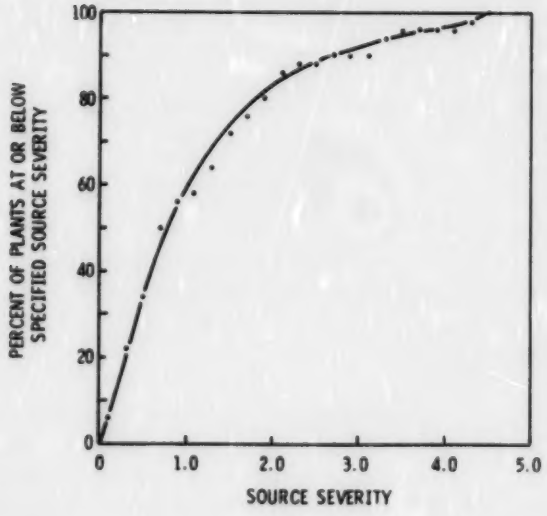

Figure 30. Source severity distribution for ammonia emissions from the granulator.

Emission	Plants with S>1
Ammonia from evaporator	100%
Ammonia from granulator	44%
Ammonia from prill tower	12%
Particulates from prill tower	40%

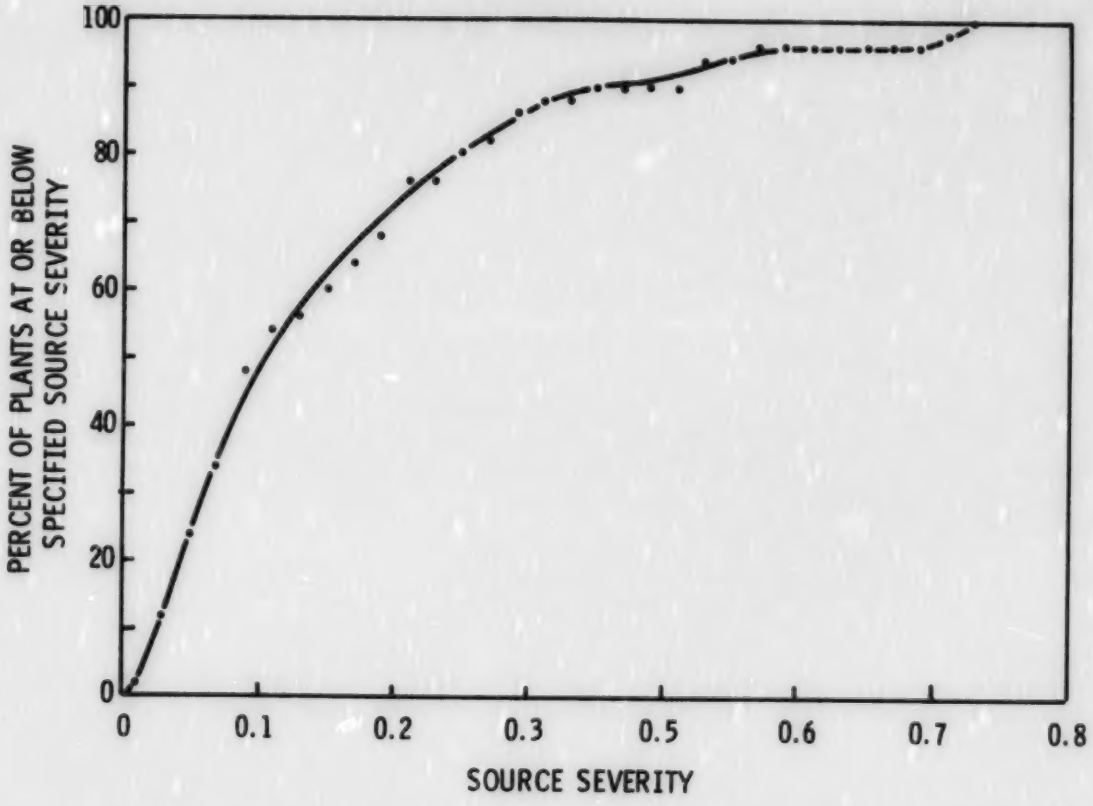

Figure 31. Source severity distribution for particulate emissions from the granulator.

3. Affected Population

The affected population is defined as the number of persons around an average urea plant who are exposed to emission concentrations that cause the ratio of χ/F to exceed 1.0. A plume dispersion equation determines the two downwind distances for which the ratio falls below 1.0 (Figure 32). The affected population is then determined by multiplying the annular area where $\chi/F > 1.0$ by the average population density (100 persons/km^2) around a representative urea plant (3, 35).

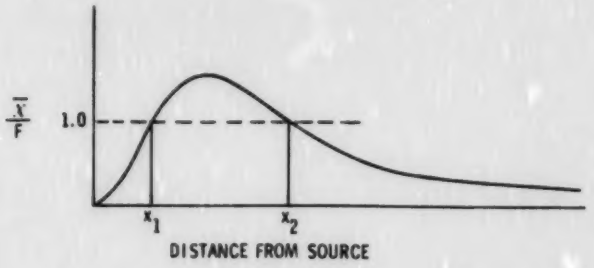

Figure 32. General distribution of $\bar{\chi}/F$ as a function of distance from the source showing the two general roots to the plume dispersion equation.

The affected population was calculated for ammonia and particulate emissions from the evaporator, prilling tower, and granulator. Results are shown in Table 12. The affected population for fugitive ammonia and particulate emissions is zero.

TABLE 12. POPULATION AFFECTED BY EMISSIONS FROM AVERAGE UREA PROCESSES

Emission point	Emission species	Affected population
Evaporator	Ammonia	247
	Particulate	0
Prill tower	Ammonia	0
	Particulate	39[a]
Granulator	Ammonia	22
	Particulate	0

[a]Affected population is greater than zero even though severity is less than 1.0 (S = 0.94) because different forms of the plume dispersion equation must be used. See References 3 and 35 for more details.

4. Particulate Emissions Burden

The environmental impact of the entire urea industry can be measured in terms of total industry emissions. Total particulate emissions are listed on a state-by-state and national basis in Table 13; they were calculated in the following manner: state production capacities were taken from the plant listing in Appendix A. Production data were derived by apportioning total urea production in 1975 according to state capacities. A total particulate emission factor was found by 1) multiplying the emission factors for each process step by the percent of total

TABLE 13. PARTICULATE EMISSION BURDEN FROM UREA PRODUCTION BY STATE

State	Capacity, 10^3 metric tons/year	Estimated 1975 production, 10^3 metric tons	Particulate emissions from urea production, metric tons/yr	Total particulate emissions from all stationary sources, 10^3 metric tons Reference 37	(Reference 36)	Percent of total particulates resulting from urea production	
Alabama	78	45.6	24.3	2,002	(1,179)	<0.01	(<0.01)
Alaska	308	180.2	95.8	16,340	(14)	<0.01	(0.68)
Arkansas	360	210.7	112.0	1,619	(138)	<0.01	(0.08)
California	441	258.1	137.2	5,675	(1,006)	<0.01	(0.01)
Florida	21	12.3	6.5	2,430	(226)	<0.01	(<0.01)
Georgia	108	63.2	33.6	2,331	(404)	<0.01	(<0.01)
Idaho	14	8.2	4.4	2,430	(55)	<0.01	(<0.01)
Illinois	77	45.1	24.0	3,584	(1,143)	<0.01	(<0.01)
Iowa	200	117.0	62.2	2,579	(216)	<0.01	(0.03)
Kansas	302	176.7	94.0	3,358	(348)	<0.01	(0.03)
Louisiana	1,640	959.7	510.4	1,651	(380)	0.03	(0.13)
Mississippi	127	74.3	39.5	1,490	(168)	<0.01	(0.02)
Missouri	153	89.5	47.6	2,839	(202)	<0.01	(0.02)
Nebraska	188	110.0	58.5	3,04[illegible]	(95)	<0.01	(0.06)
New Mexico	145	84.8	45.1	3,548	(103)	<0.01	(0.04)
New York	68	39.8	21.2	2,704	(160)	<0.01	(0.01)
North Carolina	150	87.8	46.7	2,203	(481)	<0.01	(0.01)
Ohio	263	153.9	81.8	3,054	(1,766)	<0.01	(<0.01)
Oklahoma	375	219.4	116.7	2,276	(94)	<0.01	(0.12)
Oregon	62	36.3	19.3	2,885	(169)	<0.01	(0.01)
Tennessee	472	276.2	146.9	1,789	(410)	<0.01	(0.04)
Texas	255	149.2	79.4	9,302	(549)	<0.01	(0.01)
Washington	34	19.9	10.6	2,204	(162)	<0.01	(<0.01)
Wyoming	54	31.6	16.8	2,851	(75)	<0.01	(0.02)
All other states	0	0	0	46,807	(8,329)	0	(0)
U.S. TOTAL	5,895	3,450	1,830	131,000[a]	(17,872)	0.0014	(0.010)

[a]Approximately 75% of this total is due to fugitive particulate emissions from unpaved roads.

production undergoing that operation and 2) summing these values together.

Evaporation:	62% x 0.107 g/kg	= 0.066 g/kg
Prilling:	62% x 15% x 3.2 g/kg	= 0.298 g/kg
Granulation:	62% x 85% x 0.142 g/kg	= 0.075 g/kg
Bagging and loading:	62% x 0.15 g/kg	= 0.093 g/kg
TOTAL		0.532 g/kg

Solid urea production is 62% of the total production; 15% of the solid urea product is prilled, 85% granular. Coating operations, used on less than 10% of production, were not included in the total; at most, they could increase overall particulate emissions by 20%.

The particulate emission burden for urea production is the ratio of particulate emissions from the urea industry to total particulate emissions from all sources. Different data bases can be used to obtain a state-by-state emissions inventory. Three possibilities are a 1972 emissions summary from the National Emissions Data System (NEDS) published by the EPA (36), a 1975 emissions listing assembled by Monsanto Research Corporation (37), and a 1977 emissions listing by Monsanto Research Corporation (38). The NEDS listing is the most conservative for particulate emissions since a number of open sources (i.e., not emitted from a stack) such as unpaved roads are not included in the tabulation. A 1975 NEDS summary is scheduled to be issued in late 1977, but it is not yet available. Therefore the 1975 emissions inventory by Monsanto Research Corporation was used to calculate the state emission burdens in Table 13. Emission burdens based on NEDS are also given in parentheses. On either basis, state emission burdens are all less than 1% and the national burden is less than 0.1%.

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(36) 1972 National Emission Report; National Emissions Data System (NEDS) of the Aerometric and Emissions Reporting System (AEROS). EPA-450/2-74-012, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1974. 434 pp.

(37) Reznik, R. B. Source Assessment: Flat Glass Manufacturing Plants. EPA-600/2-76-032b, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1976. 147 pp.

(38) Eimutis, E. C., and R. P. Quill. Source Assessment: State-by-State Listing of Criteria Pollutants. EPA-600/2-77-107b, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, July 1977. 138 pp.

SECTION V

CONTROL TECHNOLOGY

The use of air emission controls in urea production is concentrated in the production of solid products after the aqueous urea solution has been formed. Emissions from urea solution production are of a fugitive nature, and controls have not been applied because no state standards are exceeded. The discussion in Section IV indicates that these fugitive emissions have severities less than 1.0, beyond the plant boundary.

In the solidification process there are two steps to which control technology has been applied - solution concentration and solid formation. Controls are designed to reduce particulate emissions, while ammonia emissions are lowered only incidentally.

A. SOLUTION CONCENTRATION

In the urea industry, solutions are concentrated by crystallization and evaporation.

As mentioned in Section IV, emissions from crystallization are less than those from evaporation, and no special control devices are used. Emissions from evaporators are passed through a condenser or wet scrubbers. Although condensers lower the amount of emissions, they are not designed as air pollution control equipment, and therefore are not as effective as scrubbers.

According to industrial sources, more than 50% of urea production facilities utilize condensers to cool exhaust gases from the evaporator and condense the water vapor. A portion of the ammonia vapor and entrained particulates in the exhaust is collected in the condensate. The liquid condensate can then be sewered (when permitted), treated and recycled, sold as a dilute fertilizer solution, or sent to an adjacent facility for use in a fertilizer mixture. No data have been reported on the removal efficiencies of condensers, but they do not perform as well as wet scrubbers.

Plants without condensers use wet scrubbers to remove particulates and recover product. The scrubbing liquid is an aqueous urea solution. Tests have shown that low energy scrubbers can be over 98% efficient when operating with pressure drops of $\sim$1.5 kPa (29). Ammonia emissions are not controlled as effectively (75% removal at best; see Section IV.B.2.a). This could

be improved by using an acidic scrubbing liquid, such as a dilute urea-nitric acid solution. Since ammonia is removed from a gas stream by absorption into the scrubbing solution, removal efficiencies are strongly pH-dependent.

B. SOLID FORMATION

Solid urea is produced by either granulating or prilling the concentrated urea solution. Granulation units emit a concentrated dust stream that may contain as much as 20% of the incoming urea weight (34). High energy (3 kPa to 8kPa) wet scrubbers are used on these exhaust streams to reduce emissions and to recover valuable product for recycle. Two types of scrubbers currently in use are a venturi scrubber with a pressure drop of 4.98 kPa to 7.5 kPa (34) and a Turbulaire® scrubber with a pressure drop of 3.5 kPa. The Turbulaire scrubber has been shown to have an efficiency greater than 99.8% particulate removal (33). An aqueous solution of ammonium nitrate or urea is used as the scrubbing solution (31).

The application of wet scrubbers to granulation equipment is standard operating procedure at all plants. The efficiencies of the individual unit designs vary from facility to facility depending upon operating parameters, dust loading, particulate size and local emission regulations.

Particulate concentration, size distribution, and pressure drop differ in granulation and prilling exhaust streams. The particulate concentration in a granulator stream may be as high as 15 g/m^3. In a prilling stream (Figure 33) (34), where at least 70% of the particulates are less than 5 μm, the particulate concentration ranges from 0.6 to 1.0 g/m^3. The pressure differential in the prilling exhaust streams is usually less than 249 Pa, while the pressure drop in the granulator exhaust is usually 3.5 kPa.

Figure 33 is a compilation of size distribution studies conducted by industry (each symbol type represents a different test). Figure 34 is also a compilation of several tests; all particles larger than 5 μm were eliminated, and the material left was sized (39).

The low grain loading and small particle size present a major obstacle to reducing particulates in the prill tower exhaust. Approximately 50% of prilling installations use some form of wet scrubber in an attempt to reduce particulate emissions. The remainder use no controls. Characteristically these scrubbers

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(39) Personal communication with T. R. Metzger, Monsanto Enviro-Chem Systems, Inc., St. Louis, Missouri, 11 May 1976.

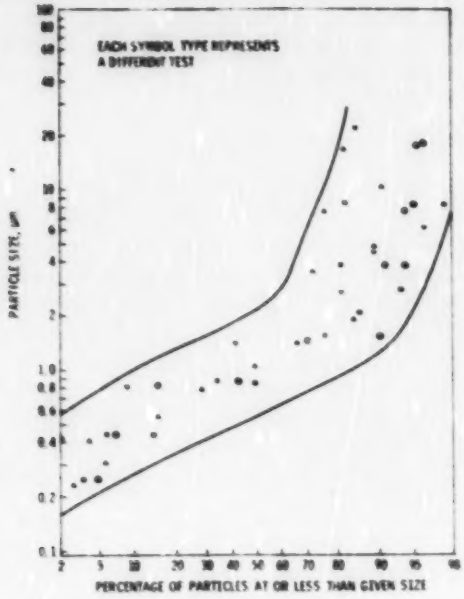

Figure 33. Size distribution of all particulates in prill tower exhaust (39).

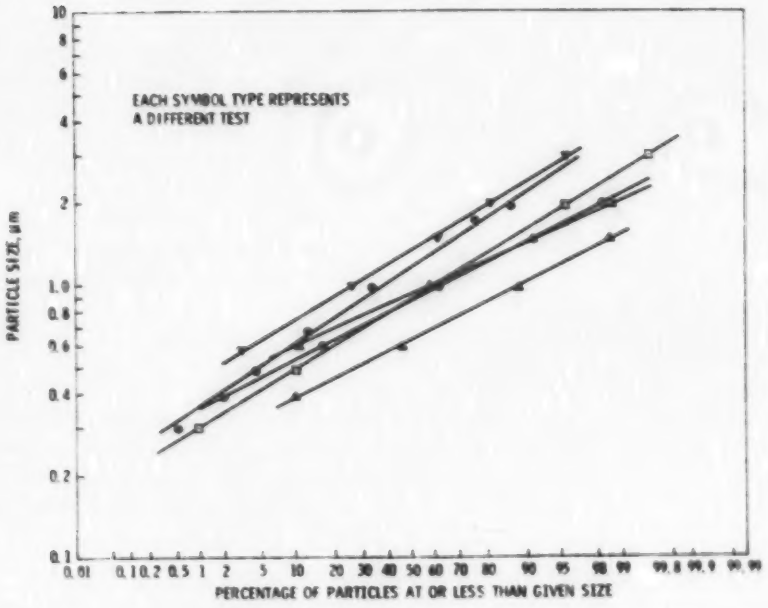

Figure 34. Size distribution of particles ≤5 µm in prill tower exhaust (39).

consist of a wetted wire mesh or other low-energy filtering medium, and a particulate removal efficiency of greater than 50% is rarely achieved.

Dutch State Mines' coal dust removal technology (34) developed a simple device which claims a higher removal efficiency than mentioned above. The dust-laden air is directed through a series of guide vanes that are sprayed with a circulating solution of urea. An 80% particulate removal has been estimated with a pressure drop of only 37.3 Pa.

Many other systems have been or are being tested on prill tower exhausts, including the following:

- Monsanto Enviro-Chem Systems' Brink® High Velocity or High Efficiency Mist Eliminators
- BECO scrubbers (e.g., Model V-2000)
- Mist-Air scrubbers
- Wet electrostatic precipitators
- Anderson 2000 CHEAF scrubber
- Fluid Ionics Hydroprecipitol
- TRW-Charged Droplet scrubber

Under normal operating conditions these scrubbers or other wet devices are expected to remove a part of the ammonia which may exist in the stream. Exact removal efficiencies depend upon operating and design parameters and local conditions.

C. FUTURE CONSIDERATIONS

The application of additional controls to urea production will be slow compared with their application to a sister industry, ammonium nitrate manuacturing, because: the applicability of several of the systems for use on prill towers has yet to be proven, and in other processes, the installed control technology is adequate to meet emission regulations and reduce product losses.

The major problem area in the industry is the control of prill tower particulate emissions to meet strict opacity regulations. Because of the high quantity of extremely small particles (Figures 33 and 34) in the exhaust stream, collection efficiencies to reduce emissions to the levels needed to meet the opacity requirements are significantly higher than those needed to meet mass emission regulations.

In other areas, such as the bulk loading of solutions and evaporation, available techniques could further reduce emissions. For example, acidic scrubbing solutions can be used for better control of ammonia emissions. Other possibilities are the use of floating roofs and other techniques developed by the petroleum industry to reduce hydrocarbon losses from storage tanks. These controls are not presently employed because the emissions from these points do not violate state standards and because product losses are not excessive.

D. POTENTIAL IMPACT OF CONTROLS

The greatest potential impact of control technology would result from better control of particulate emissions from prill towers and ammonia emissions from evaporators and granulators. If particulate emissions from the prill tower were controlled by 95%, the resulting average source severity would be 0.05. A reduction in ammonia emissions from the evaporator and granulator by an additional 99% would result in average severities of 0.088 and 0.013, respectively.

SECTION VI

GROWTH AND NATURE OF THE INDUSTRY

A. PRESENT TECHNOLOGY

Urea production technology is well established with no major process changes anticipated. Each company has its own modification of the basic design based upon individual plant operation.

B. EMERGING TECHNOLOGY

Energy conservation is the first area of emerging technology for the urea industry. There are two major new energy conserving processes. Mitsui Toatsu has developed a process for heat exchange between the urea process and the ammonia process to effect overall heat conservation (7). Several other companies including SNAM PROGETTI are investigating similar processes (17).

A second energy conserving process is the Mavrovic "Heat Recycle" urea process (40, 41). This process uses an isothermal reactor, specialized decomposers, and strippers designed to achieve higher yield, lower utility costs, and ease of control. Internal heat recovery and exacting operation are key elements in this process.

A second area of emerging technology lies in derivations from traditional flow and processing elements. One of these is the Chemico Thermo-Urea process (Figure 35) which uses a multistage centrifugal compressor to decompose carbamate and recycle it to the reactor. This process also recovers steam, which is a utility savings.

Esso Research and Engineering Co. has also developed a process that departs from the traditional. This process synthesizes urea at traditional temperatures; however, it incorporates the decomposer/stripper and the reactor into a single unit.

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(40) The Mavrovic "Heat Recycle: Urea Process. Nitrogen, 78:19-21, July/August 1972.

(41) Mavrovic, I. Improved Urea Process is Developed. Chemical Engineering Progress, 70(2):69, 71, 73, 1974.

These new processes do not affect the overall environmental air impact of urea manufacture, since they are all involved with the solution production stage.

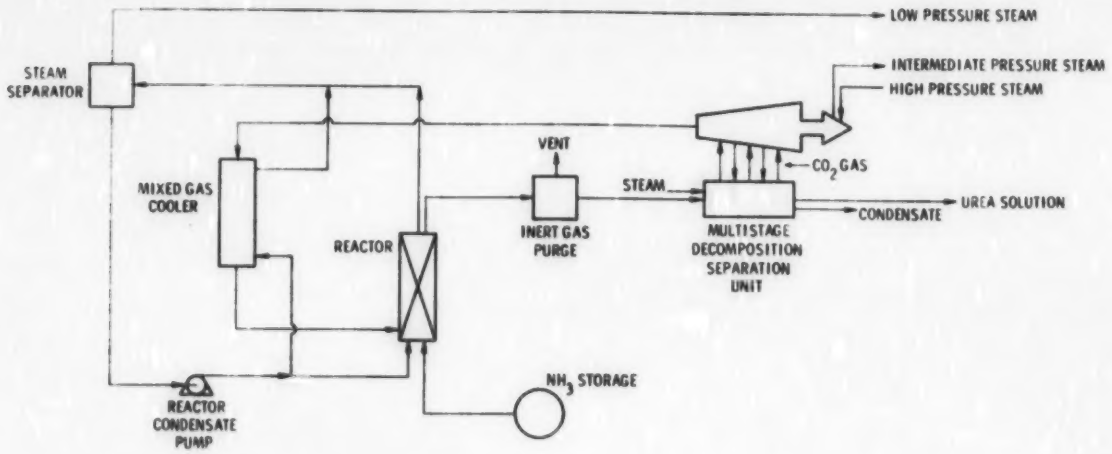

Figure 35. Chemico Thermo-Urea process.

C. INDUSTRY PRODUCTION TRENDS

Figure 36 illustrates the actual growth in the urea industry from 1960 through 1975 and projected growth through 1980. Historical production information is available from the U.S. Tariff Commission and the U.S. International Trade Commission (42-56). Projected capacities are based on known plans for construction (7). Projected production is based on 87.1% of projected capacity. (The 87.1% value was determined by averaging production/capacity ratios from 1960 through 1975.)

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(42) Synthetic Organic Chemicals, United States Production and Sales, 1960. TC Publication 34, United States Tariff Commission, Washington, D.C., 1961. p. 58.

(43) Synthetic Organic Chemicals, United States Production and Sales, 1961. TC Publication 72, United States Tariff Commission, Washington, D.C., 1962. p. 56.

(44) Synthetic Organic Chemicals, United States Production and Sales, 1962. TC Publication 114, United States Tariff Commission, Washington, D.C., 1963. p. 59.

(45) Synthetic Organic Chemicals, United States Production and Sales, 1963. TC Publication 143, United States Tariff Commission, Washington, D.C., 1964. p. 58.

(continued)

Urea production is anticipated to increase at a rate of 4.7% to 8% per year (5). This growth will be promoted by three factors: 1) domestic melamine production has switched from dicyandiamide to urea as a raw material, 2) prilled urea is being promoted as a fertilizer export, and 3) research is being conducted in forest fertilization using urea as the fertilizer. As a result of this growth, emissions from the industry in 1978 should be 32% to 59% greater than in 1972.

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(46) Synthetic Organic Chemicals, United States Production and Sales, 1964. TC Publication 167, United States Tariff Commission, Washington, D.C., 1965. p. 59.

(47) Synthetic Organic Chemicals, United States Production and Sales, 1965. TC Publication 206, United States Tariff Commission, Washington, D.C., 1965. p. 59.

(48) Synthetic Organic Chemicals, United States Production and Sales, 1966. TC Publication 248, United States Tariff Commission, Washington, D.C., 1968. p. 58.

(49) Synthetic Organic Chemicals, United States Production and Sales, 1967. TC publication 295, United States Tariff Commission, Washington, D.C., 1969. p. 56.

(50 Synthetic Organic Chemicals, United States Production and Sales, 1968. TC Publication 327, United States Tariff Commission, Washington, D.C., 1970. p. 213.

(51) Synthetic Organic Chemicals, United States Production and Sales, 1969. TC Publication 412, United States Tariff Commission, Washington, D.C., 1971. p. 203.

(52) Synthetic Organic Chemicals, United States Production and Sales, 1970. TC Publication 479, United States Tariff Commission, Washington, D.C., 1972. p. 211.

(53) Synthetic Organic Chemicals, United States Production and Sales, 1971. TC Publication 614, United States Tariff Commission, Washington, D.C., 1973. p. 204.

(54) Synthetic Organic Chemicals, United States Production and Sales, 1972. TC Publication 631, United States Tariff Commission, Washington, D.C., 1974. p. 203.

(55) Synthetic Organic Chemicals, United States Production and Sales, 1973. ITC Publication 728, United States International Trade Commission, Washington, D.C., 1975. p. 201.

(56) Synthetic Organic Chemicals, United States Production and Sales, 1974. USITC Publication 776, United States International Trade Commission, Washington, D.C., 1976. p. 199.

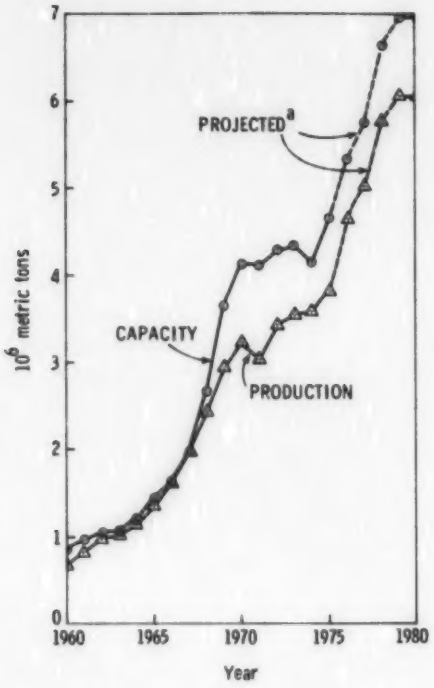

Figure 36. Urea capacity and production trends (42-56).

[a]Capacity projection based on announced or anticipated expansions or new facilities. Production projection based on an 87.1% operating rate.

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TABLE A-1. LOCATION, POPULATION DENSITY, AND CAPACITY DATA FOR UREA PLANTS IN THE U.S. (7)

Company	City/state	County, parish, or borough: Name	County, parish, or borough: Population density, persons/km^2	Annual capacity, 10^3 metric tons
Air Products and Chemicals, Inc.	Pace, Fla.	Escambia	116.6	21
Allied Chemical Corp., Union Texas Petroleum Division				
Agricultural Department	Geismar, La.	Ascension	46.7	222
	Omaha, Nebr.	Douglas	446.3	127
Specialty Chemicals Division	South Point, Ohio	Lawrence	47.0	63
American Cyanamid Co.	Fortier, La.	Jefferson	393.6	132
Beker Industries Corp.	Carlsbad, N. Mex.	Eddy	3.7	145
Borden, Inc. - Borden Chemical Division	Geismar, La.	Ascension	46.7	200
California Oil Purification Co.	Ventura, Calif.	Ventura	77.6	120
CF Industries, Inc.	Donaldsonville, La.	Ascension	46.7	329
	Fremont, Nebr.	Dodge	25.3	16
	Olean, N.Y.	Cattaraugus	23.4	68
	Tunis, N.C.	Hertford	24.5	150
	Tyner, Tenn.	Hamilton	170.3	30
Cherokee Nitrogen Co.	Pryor, Okla.	Mayes	12.8	16
Coastal States Gas Corp., Colorado Interstate Corp., subsidiary; Wycon Chem. Co., subsidiary	Cheyenne, Wyo.	Laramie	7.9	54
Columbia Nitrogen Corp.	Augusta, Ga.	Richmond	192.3	35

(continued)

TABLE A-1 (continued).

Company	City/state	County, parish, or borough: Name	County, parish, or borough: Population density, persons/km^2	Annual capacity, 10^3 metric tons	
Enserch Corp., Nipak, subsidiary	Kerens, Tex.	Navarro	10.8	63	
	Pryor, Okla.	Mayes	12.8	93	170
	Pryor, Okla.	Mayes	12.8	77	
Esmark, Inc.	Beaumont, Tex.	Jefferson	98.5	45	
Farmland Industries, Inc., Cooperative Farm Chemicals Assoc. (CFCA)	Dodge City, Kans.	Ford	7.8	58	
	Lawrence, Kans.	Douglas	38.6	244	
	Lawrence, Kans.	Douglas	38.6		
Gardiner Big River, Inc.	Helena, Ark.	Phillips	22.3	61	
General American Oil of Texas	Pasadena, Tex.	Harris	385.9	85	
	Pasadena, Tex.	Harris	385.9		
Goodpasture, Inc.	Dimmitt, Tex.	Castro	4.5	21	
W. R. Grace & Co.	Memphis, Tenn.	Shelby	367.6	125	442
	Memphis, Tenn.	Shelby	367.6	317	
Hercules, Inc.	Hercules, Calif.	Alameda	557.8	18	36
	Hercules, Calif.	Alameda	557.8	18	
	Louisiana, Mo.	Pike	9.4	32	86
	Louisiana, Mo.	Pike	9.4	54	
Kaiser Aluminum and Chemical Corporation	Savannah, Ga.	Chatham	158.7	73	
Mississippi Chemical Corporation	Yazoo City, Miss.	Yazoo	11.2	127	
	Yazoo City, Miss.	Yazoo	11.2		

(continued)

TABLE A-1 (continued).

Company	City/state	County, parish, or borough: Name	County, parish, or borough: Population density, persons/km^2	Annual capacity, 10^3 metric tons
N-Ren Corp., (see also Cherokee Nitrogen Co., and St. Paul Ammonia Products, Inc.)	Plainview, Tex.	Hale	13.2	41
Olin Corp., Agricultural Chemicals Division	Lake Charles, La.	Calcasieu	49.7	150
Phillips Pacific Chemical Co.	Finley, Wash.	Benton	14.9	34
	Finley, Wash.	Benton	14.9	
Phillips Petroleum Co.	Beatrice, Nebr.	Gage	11.6	45
	Beatrice, Nebr.	Gage	11.6	
Reichold Chemicals, Inc.	St. Helen, Oreg.	Columbia	17.2	62
St. Paul Ammonia Products, Inc.	East Dubuque, Ill.	Jo Daviess	13.5	77
J. R. Simplot Co.	Pocatello, Idaho	Bannock	17.5	14
Skelly Oil Co., Hawkeye Chemical Co., subsidiary	Clinton, Iowa	Clinton	31.3	55
Standard Oil Co., (Ohio) - Vistron Corp., - subsidiary	Lima, Ohio	Allen	104.4	200
Tennessee Valley Authority	Muscle Shoals, Ala.	Colbert	31.8	55
Terra Chemicals International, Inc.	Port Neal, Iowa	Woodbury	44.6	145
	Port Neal, Iowa	Woodbury	44.6	
Triad Chemical	Donaldsonville, La.	Ascension	46.7	426
	Donaldsonville, La.	Ascension	46.7	

(continued)

TABLE A-1 (continued).

Company	City/state	County, parish, or borough: Name	County, parish, or borough: Population density, persons/km^2	Annual capacity, 10^3 metric tons	
Tyler Corporation-Atlas Powder Co., subsidiary	Joplin, Mo.	Jasper	47.3	67	
Union Oil Company of California-Collier Carbon and Chemical Corp., subsidiary	Brea, Calif.	Orange	695.8	109	
	Kenai, Alaska	Kenai Pen.	0.5	308	
United States Steel Corporation, USS Agri-Chemicals, Division	Cherokee, Ala.	Colbert	31.8	23	
Valley Nitrogen Producers, Inc.	El Centro, Calif.	Imperial	6.7	135	
	Helm, Calif.	Fresno	26.3	19	41
	Helm, Calif.	Fresno	26.3	22	
The Williams Companies Agrico Chem. Co., subsidiary	Blytheville, Ark.	Mississippi	26.3	299	
	Donaldsonville, La.	Ascension	46.7	181	
	Verdigris, Okla.	Rogers	14.9	190	
TOTAL				5,895	

APPENDIX B

DERIVATION OF AVERAGING EQUATIONS

When the average emission factor for a source must be determined from a collection of average values, an averaging procedure must be devised since previously used concepts are not applicable. The following rationale was used to determine Equations 7 and 8 in Section IV.B.3 of the text.

Let m be the number of aggregate samples, with each sample having a certain number of points (n_i). An average for all of the points ($\bar{x}_i$) within a given sample can be calculated by the following equation:

$$\bar{x}_i = \frac{\sum_{j=1}^{n_i} x_j}{n_i} \qquad \text{(B-1)}$$

where x_j = the value of a point in the i-th sample

The standard deviation can be calculated according to the following equation:

$$s_i^2 = \frac{\sum_{j=1}^{n_i} (x_j - \bar{x}_i)^2}{n_i - 1} \qquad \text{(B-2)}$$

If each data point, x_j, for every sample were identifiable, the average for the entire group of samples could be found by summing the entire set of points and dividing by the total number of points as follows:

$$\bar{x}_T = \frac{\sum_{i=1}^{m} \sum_{j=1}^{n_i} x_j}{\sum_{i=1}^{m} n_i} \qquad \text{(B-3)}$$

However, since the exact data points are not identifiable, only the averages and total number of points for each sample, Equation B-1, can be rearranged and substituted into B-3, giving:

$$\bar{x}_T = \frac{\sum_{i=1}^{m} n_i \bar{x}_i}{\sum_{i=1}^{m} n_i} \qquad \text{(B-4)}$$

To determine the standard deviation for "i" samples we must first rearrange and expand Equation B-2.

$$s_i^2 (n_i - 1) = \sum_{j=1}^{n_i} (x_j - \bar{x}_i)^2$$

$$= \sum_{j=1}^{n_i} x_j^2 - 2\bar{x}_i \sum_{j=1}^{n_i} x_j + \sum_{j=1}^{n_i} \bar{x}_i^2 \qquad \text{(B-5)}$$

By rearranging Equation B-1 and substituting into Equation B-5:

$$s_i^2 (n_i - 1) = \sum_{j=1}^{n_i} x_j^2 - 2n_i \bar{x}_i^2 + \bar{x}_i^2 n_i$$

$$= \sum_{j=1}^{n_i} x_j^2 - n_i \bar{x}_i^2 \qquad \text{(B-6)}$$

Rearranging,

$$\sum_{j=1}^{n_i} x_j^2 = s_i^2 (n_i - 1) + n_i \bar{x}_i^2 \qquad \text{(B-7)}$$

If each data point, x_j, for every sample were identifiable, the standard deviation for the entire group of samples, s_T, could be found by the following equation:

$$s_T^2 = \frac{\sum_{i=1}^{m}\sum_{j=1}^{n_i}(x_j - \bar{x}_T)^2}{\left(\sum_{i=1}^{m} n_i\right) - 1} \qquad \text{(B-8)}$$

Since

$$\sum_{i=1}^{m}\sum_{j=1}^{n_i}(x_j - \bar{x}_T)^2 = \sum_{i=1}^{m}\left(\sum_{j=1}^{n_i} x_j^2 - 2\bar{x}_T\sum_{j=1}^{n_i} x_j + \bar{x}_T^2\sum_{j=1}^{n_i} 1\right)$$

$$= \sum_{i=1}^{m}\left(\sum_{j=1}^{n_i} x_j^2 - 2\bar{x}_T^2 n_i + \bar{x}_T^2 n_i\right)$$

$$= \sum_{i=1}^{m}\sum_{j=1}^{n_i} x_j^2 - \sum_{i=1}^{m} n_i\bar{x}_T^2 \qquad \text{(B-9)}$$

Then

$$s_T^2 = \frac{\sum_{i=1}^{m}\sum_{j=1}^{n_i} x_j^2 - \bar{x}_T^2\sum_{i=1}^{m} n_i}{\left(\sum_{i=1}^{m} n_i\right) - 1} \qquad \text{(B-10)}$$

By substituting Equation B-7 into B-10 the following equation is determined:

$$s_T^2 = \frac{\sum_{i=1}^{m} s_i^2 (n_i - 1) + \sum_{i=1}^{m} n_i \bar{x}_i^2 - \bar{x}_T^2 \sum_{i=1}^{m} n_i}{\left(\sum_{i=1}^{m} n_i\right) - 1} \qquad \text{(B-11)}$$

Or

$$s_T = \left[\frac{\sum_{i=1}^{m} s_i^2 (n_i - 1) + \sum_{i=1}^{m} n_i \bar{x}_i^2 - \bar{x}_T^2 \sum_{i=1}^{m} n_i}{\left(\sum_{i=1}^{m} n_i\right) - 1} \right]^{1/2} \qquad \text{(B-12)}$$

Equation B-12 is the same as Equation 8 shown in Section IV.B.3 of the text.

GLOSSARY

additive: Any material added to the concentrated urea before solids formation which changes the natural mechanical characteristics of the solid urea particle.

affected population: Number of persons living in the area near an average process where the source severity is greater than 1.0.

biuret ($(NH_2CO)_2NH$): Impurity formed when solid urea is heated above 130°C at atmospheric pressure.

coating: Any material placed externally on a prill or granule designed to enhance shelf-life and reduce hygroscopicity.

crystallizer: Equipment in which a crystalline solid is formed from the liquid urea by using the sensible heat of the solution and the heat of crystallization.

emission factor: Mass of an emission per unit weight of final product.

emission growth factor: Ratio of emissions for 1978 versus 1972.

emission rate: Mass of emissions per unit time.

evaporator: Equipment in which the liquid urea is concentrated by passing it countercurrent to an air stream.

granulator: Equipment in which concentrated urea solution is solidified by spraying the concentrated solution on a falling curtain or rolling bed of seed particles to build a larger particle.

granules: Solid urea particles formed by applying molten urea to fine urea seed particles to increase the particle size in a layered fashion.

national emission burden: Mass of particulates emitted from urea manufacturing divided by the total national particulate emissions expressed in percent.

once-through process: Urea solution process in which there are no recycle streams of unreacted reactants.

partial recycle process: Urea solution process in which only excess ammonia is recovered and recycled to the reactor.

phytotoxic: Poisonous to plant life.

prill, micro: Small size prills or prill tower screenings used for blending with livestock feed.

prill, standard: Solid urea particle formed when a drop of liquid urea is solidified.

prilling: Process in which concentrated urea solution is solidified by spraying the concentrated solution in a tower so that the drops formed fall countercurrent to a stream of cooling air.

source severity: Ratio of the ground level concentration of each emission species to its corresponding ambient air quality standard (for criteria pollutants) or to a reduced TLV (for noncriteria emission species).

Spherodizer®: Specific make of drum granulator.

state emission burden: Mass of particulates emitted from the ammonium nitrate industry in a particular state divided by the total state particulate emissions expressed in percent.

threshold limit value (TLV): Refers to the airborne concentration of a substance and represents conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse effect for a 7- or 8-hour workday and 40-hour workweek.

total recycle process: Process utilizing excess ammonia recycle plus recycle of unreacted reactants as a gas or in a liquid carbamate form.

CONVERSION FACTORS AND METRIC PREFIXES (57)

CONVERSION FACTORS

To convert from	to	Multiply by
degree Celsius (°C)	degree Fahrenheit	$t_{°F} = 1.8\ t_{°C} + 32$
degree Kelvin (K)	degree Celsius	$t_{°C} = t_{°K} - 273.15$
gram/second (g/s)	pounds/hour	7.936
joule (J)	calorie	2.388×10^{-1}
kilogram (kg)	pound-mass (lb mass avoirdupois)	2.204
kilogram/meter^3 (kg/m^3)	pound/foot^3	6.243×10^{-2}
kilometer^2 (km^2)	mile^2	3.860×10^{-1}
meter (m)	foot	3.281
meter^2 (m^2)	foot^2	1.076×10^{1}
metric ton	pound-mass	2.205×10^{3}
metric ton	ton (short, 2,000 lb-mass)	1.102
pascal (Pa)	atmosphere	9.869×10^{-6}
pascal (Pa)	torr (mm Hg, 0°C)	7.501×10^{-3}
pascal (Pa)	pound-force/inch^2 (psi)	1.450×10^{-4}
radian (rad)	degree (°)	5.730×10^{1}

METRIC PREFIXES

Prefix	Symbol	Multiplication factor	Example
mega	M	10^6	1 MPa = 1 x 10^6 pascals
kilo	k	10^3	1 kJ = 1 x 10^3 joules
centi	c	10^{-2}	1 cm = 1 x 10^{-2} meter
milli	m	10^{-3}	1 mg = 1 x 10^{-3} gram
micro	μ	10^{-6}	1 μm = 1 x 10^{-6} meter

(57) Standard for Metric Practices. ANSI/ASTM Designation E 380-76$^{\varepsilon}$, IEEE Std 268-1976, American Society for Testing and Materials, Philadelphia, Pennsylvania, February 1976. 37 pp.